United States Court of Appeals

for the Second Circuit

APPENDIX

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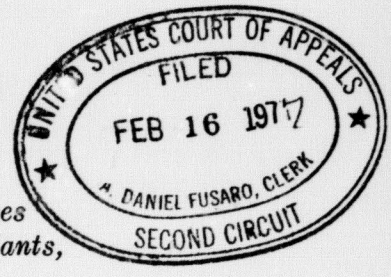
United States Court of Appeals
For the Second Circuit



EUTECTIC CORPORATION, NEW METALS CORPORATION and METALLIZING COMPANY OF AMERICA, INC.,

Plaintiffs-Appellees and Cross-Appellants,

v.

METCO, INC.,

Defendant-Appellant and Cross-Appellee.

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VOLUME VI OF EIGHT VOLUMES

(EXHIBITS — Pages E242 to E598)

HOPGOOD, CALIMAFDE, KALIL, BLAUSTEIN & LIEBERMAN
Attorneys for Plaintiffs-Appellees and Cross-Appellants
60 East 42nd Street
New York, New York 10017
(212) 986-2480

BURGESS, DINKLAGE & SPRUNG
Attorneys for Defendant-Appellant and Cross-Appellee
600 Third Avenue
New York, New York 10016
(212) 661-0520

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P. R. Div.

Class

Filed Complete (Date)
AUG. 16, 1951

3254970

DATED

PATENT NUMBER

Number claims allowed
14

Print claimed

Drawing

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...FERDINAND J. ... OF BELLMORE, ...

...ARTHUR P. ... OF FLUSHING, N. ...

...tes, Inc., a corp. of New Jersey

...ING SYNERGISTIC COMPOSITES

Division of

Continuation of

Substitute for abandoned

APPLICATION

Serial No.

Filed

Filing Fee

Examiner

Art Unit

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BURGESS, DINKLAGE & SPRUNG
Attorneys
233 BROADWAY
NEW YORK 7, N. Y.

E 243
134544

Date: August 15, 1961

Hon. Commissioner of Patents
Washington 25, D. C.

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Dear Sir:

Re the application of [illegible]

for [illegible]

we enclose

(x) Specification

(x) Oath, Power of Attorney and Petition

( ) 1 Sheet(s) Drawings*

(x) 11 Claim(s) in excess of 20

(x) $ 11.00 filing fee (covered by enclosed check)

( ) Assignment

( ) $3.00 recording fee (covered by enclosed check)

( ) Priority is hereby claimed on the basis of the following:

Country	Serial No.	Date
[illegible]	[illegible]	[illegible]

[illegible] Serial No. 72 543, [illegible]

Respectfully,

BURGESS, DINKLAGE & SPRUNG

BY [signature]

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E 244

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FLAME SPRAYING SYNERGISTIC COMPOSITES

This invention relates to the flame spraying of synergistic composites. The invention more particularly relates to the flame spraying of synergistically-clad flame spray powders, to a novel group of flame spray materials comprising such synergistically-clad flame spray powders, and more broadly to the spraying of other synergistic composites wherein the synergistic action involves the generation of heat.

Flame spraying involves the feeding of a heat-fusible material into a heating zone, wherein the same is melted or at least heat-softened and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone formed by a flame of some type, where it is melted or at least heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by

sintering together finely divided material or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun, as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly produced from a flame caused by the combustion of a fuel, such as acetylene, propane, natural gas or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or in the newer type of guns, by a plasma flame. The plasma

flame may in itself constitute part of an electric arc or, in accordance with a newer development, may be in the form of a "free plasma stream", i.e., a stream of plasma which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead and zinc.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic or the like. While it is true that rods or wires formed from finely divided material bound together with a binder of plastic or the

like, as mentioned above, were known, the binder did not take part in the spraying or contribute to the coating and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form, which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spraying materials.

These and still further objects will become apparent from the following description read in conjunction with the drawings in which:

Fig. 1 diagrammatically shows a cross-section of a grain of a novel flame spray powder in accordance with the invention;

Fig. 2 is a diagrammatic cross-section of a further embodiment of a grain of a novel flame spray powder in accordance with the invention;

Fig. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray rod or wire in accordance with the invention; and

Fig. 4 shows an elevation of a further embodiment of a novel flame spray rod or wire in accordance with the invention.

In accordance with a broad aspect of the invention the flame spraying is effected with the material being sprayed in the form of a powder, the individual grains of which are in the form of a clad composite consisting of nuclei and at least one coating layer of a different material which will synergistically act with the nuclei in the process.

Each grain of the synergistically clad composite powders may also be in the form of a nucleus with two or more different coating layers which will synergistically act with each other and/or with the nucleus.

The synergistic action of the coating layer with the nucleus and the coating layers with each other, as the case may be, may manifest itself as a chemical or physical action or both, and may appear in the heating zone and/or along the path of travel to the surface to be coated, or at the sprayed coating as sprayed, or after a subsequent treatment such as a heating or fusing operation.

The synergistic action between the nuclei and/or the coating layer or layers may, for example, involve the physical or chemical generation of heat by exothermic reaction in the heating zone, along the path of travel to the target, or on the coated surface itself, so as to

increase the thermal efficiency of the process, aid in the bonding of the coating and/or produce results and effects by this *in situ* generated heat which cannot be achieved by the externally supplied heat. The synergism resulting in the exothermic reaction may be caused by the utilization of two components which will combine at the temperatures involved to form a material with a melting point higher than that of either of the constituents, with a considerable release of heat, by the use of components which will chemically combine in exothermic reaction, as for example where one acts as an oxidizing and the other a reducing agent, or by the use of components which will dissolve together in generation of heat or the like.

Thus, for example, one of the components may be a nickel-containing component and the other an aluminum-containing component which will combine under the spraying conditions to form a nickel-aluminum inter-metallic compound with an exothermic reaction. Similarly, one of the components may contain the aluminum and the other antimony, calcium, cobalt, lanthanum, lithium, manganese, nickel, palladium, praseodymium, dysprosium, or a combination thereof which, upon combining during the spraying, form a higher melting point compound with the generation of heat. Similarly the clad-composite powder may be a combination of nickel with elemental phosphorus, silver, copper, aluminum or the like, which will combine in exothermic reaction.

The synergistic action may also involve a protective effect of the coating material on the nuclei or a lower coating layer in order to prevent loss or destruction of this under-material and allow the spraying of the combination. Thus, for example, nickel may be coated on nickel-phosphorus, nickel-boron, or the like in order to prevent loss or destruction of the fluxing agent and allow the formation of a self-fluxing coating, as for example in the "spray-weld process."

The synergism may also involve a bonding effect in order to allow a satisfactory bonding on a base of sprayed materials which normally present bonding difficulties, as for example the synergism of a matrix metal, such as nickel or cobalt, with a hard or refractory material, such as tungsten carbide, Al_2O_3, diamonds or other hard gems or the like.

Bonding to the base or substrate being coated may also be aided by the synergistic action of exothermic reaction, as for example in the case of nickel-coated aluminum powder.

The synergistic effect may also involve the combining of the components to form a third component, such as a compound or alloy or inter-metallic compound desired as the coating constituent. This may involve a dissolving together of the components, alloying the components, or a chemical reaction between components which may be endothermic in nature if sufficient heat is available for the process.

The powder particles may be in the form of a nucleus with a single coating layer, or may be in the form of a nucleus with a multiple number of layers of the same or different materials.

The clad powders in accordance with the invention may be formed in any known or desired manner and preferably by the known chemical plating processes in which a coating material is deposited on a seed or nucleus of another material, or in which multiple layers of various materials are built up on the seed material, or in which various materials are co-deposited in a single layer on the seed material.

A preferred mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulphate on a seed powder catalyzed by the addition of anthraquinone. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor deposition, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal decomposition of halides, hydrides, carbonyls, organo-metals or other volatile compounds, or by displacement gas plating and the like.

The clad powders for this invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a

size between -60 mesh and +3 microns and preferably -140 and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the clad powders may be sprayed per se or in combination with other different clad powders, or in combination with other conventional flame spray powders or powder components.

Fig. 1 diagrammatically shows an embodiment of a clad powder having a nucleus of aluminum and a coating of nickel.

Fig. 2 shows a multi-layer powder of nickel and copper on nickel-boron.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder which decomposes in the heating zone of the gun,or, in certain cases the powders may be compacted and/or sintered together in the form of a rod or wire.

In the limited case where the synergistic action of the components involves an exothermic reaction as, for example, the combination of nickel and aluminum to form the nickel-aluminum inter-metallic compounds, the

spray material may assume a form other than the clad powder and may, for example, be in the form of a suitable aggregate or a composite wire, such as a wire having a coating sheath of one material, such as nickel, with a core of the other material, such as aluminum, as shown in Fig. 3, or wire formed by twisting together and rolling separate wires of components, such as nickel and aluminum, as shown in Fig. 4. Various combinations of other exothermically-reacting components may of course be used in the formation of such wire, which exothermic reaction will substantially contribute to the heat economy of the flame spraying and may even show self-ignition characteristics when fed through the spray gun.

The following examples are given by way of illustration and not limitation:

EXAMPLE 1

An aluminum powder having a particle size between -140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate, using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 300 and 350° F. in a mechanically agitated autoclave using solutions containing 40-50 grams per liter of nickel and 10-400 grams per liter of $(NH_4)_2SO_4$ and 20-30 grams

per liter of NH_3. About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i.g. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder is formed containing about 16 to 18% by weight aluminum and 84 to 82% by weight of nickel, and a size of -100 to +270 mesh.

The powder thus formed is flame-sprayed on a mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 7 inches from the plate, using a powder-type flame-spray gun as described in U. S. Patent 2,961,335, issuing November 22, 1960 and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermospray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel at a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu.ft./hr.

and oxygen as the oxidizing gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu.ft./hr.

The nickel coating and the aluminum base combine in the heat of the flame with a strong exothermic action, forming a nickel aluminum inter-metallic compound which deposits on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002" - .004" thickness is built up in this manner. The coating may be used as a base material for spraying of further layers of different metals or the like and serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .004" - .008", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020" - .040" or thicker as a wear-resistant - oxidation-resistant surface.

Due to its self-bonding characteristics the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the

powder has excellent oxidation-r istant characteristics even at high temperatures and in oxidizing atmospheres, and will for example eliminate the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature, wear-resistant coatings.

When the example is repeated on a molybdenum rod of 3/16" diameter, with a coating between .008" - .010" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, with a welding torch, and cooled to room temperature with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10 - 45% by weight of aluminum and 55 - 90% by weight of nickel.

EXAMPLE 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough ground or light-grit-blasted; and titanium, rough-ground or light-grit-blasted.

In each case when a further material, such as steel, alumina or the like, was sprayed over the coating in the conventional and well known manner, the same was bonded with a tenacious bond, though if this material had been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

EXAMPLE 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface-cleaned by smooth grinding. Spraying is effected at a distance of about 7" from the plate at a rate of about 4 to 8

lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17 - 25 cu.ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29 - 35 cu.ft./hr.

A self-bonding cermet coating is formed which showed excellent thermal shock-resistance, hardness, abrasion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an increased amount of the inter-metallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

EXAMPLE 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium

zirconate, spinel, ceric oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium silicide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

EXAMPLE 5

A nickel-phosphorus powder having a size between 200 and 325 mesh and containing 8 to 12% phosphorus is coated with nickel to form a composite-clad powder having a size between 140 and 270 mesh and containing 20 to 40% of the nickel phosphorus nucleus and 60 to 80% of the nickel coating.

The powder is sprayed in the identical manner described in Example 1. The coating obtained is mechanically bonded to the base and is slightly porous. This coating may be subsequently fused by a welding torch or furnace heated to form a homogenous pore-free coating welded to the base material.

EXAMPLE 6

A nickel-boron powder is coated with nickel to form a composite flame-spray

powder having a size between 120 and 325 mesh and containing 70 to 90% nickel, based on the nickel boron. The powder was sprayed in the manner described in Example 1 and a high quality of self-fluxing coating was formed.

The coating is mechanically bonded to the base and may be subsequently fused with a welding torch or in a furnace to form a dense homogenous, non-porous coating. When applied to a reactive base material, such as molybdenum, in a thickness of .006" to .010" or heavier, the coating can be fused to the base material by a torch or furnace without atmosphere control and below the recrystallization temperature of pure molybdenum, and will protect the molybdenum base from an oxidizing atmosphere at elevated temperatures up to the melting point of the nickel-boron coating.

EXAMPLE 7

Metallic cobalt is deposited as a coating on zirconia powder by the reduction of a cobalt ammonium sulphate solution with hydrogen so as to form a cobalt-clad zirconia flame-spray powder having a size between

325 mesh and 15 microns and containing 25 to 95% cobalt, based on the zirconia. The material is sprayed in the manner described in Example 1 on a grit-blasted base and a cermet coating is formed which shows excellent adhesion to the base and which will retard oxidation of the base. The coating furthermore has a high degree of hardness even at elevated temperatures, excellent shock-resistance and abrasion-resistance, and the metal matrix material is evenly distributed throughout the applied coating.

It is possible to vary the percentages of the ceramic in the composition between about 5 and 75% by weight in order to vary the properties of the coating. With an increased amount of ceramic in the cermet coating, the hardness and wear-resistant properties of the coating are correspondingly increased and the thermal conductivity decreased. Conversely, with an increasing amount of the cobalt matrix the bonding and shock-resistant properties are increased.

EXAMPLE 8

Al_2O_3 powder of a mesh size between 80 microns and 10 microns is coated with nickel in the manner described in Example 1 to produce a composite powder containing 25 to 95% of the nickel based on the aluminum oxide and having a particle size beteen 140 mesh and 15 microns. The powder is sprayed in the manner described in Example 1 on a grit-blasted base, and a cermet coating is formed which shows excellent adhesion to the base, a high degree of hardness even at elevated temperatures, and excellent thermal shock and abrasion-resistant characteristics. The metal matrix is evenly distributed throughout the sprayed coating.

In this case too it is possible to vary the percentage of the ceramic in the composite between 5 and 75% by weight, and with an increasing amount of ceramic, the hardness and wear-resistant properties increase, whereas with an increase of the nickel, the thermal conductivity, bonding and shock-resistant properties are increased.

EXAMPLE 9

Industrial diamond powder having a size between -120 and +140 mesh was coated with nickel in the manner described in Example 1 so that the nickel-clad composite powder formed contained about 25 to 50% by weight of the nickel, based on the diamonds. The powder was sprayed in the manner described in Example 1 on a steel base prepared by grit blasting, thus forming an excellent hone or lap in which the diamonds were firmly bonded in place.

EXAMPLE 10

Cobalt-bonded tungsten carbide particles of sharp, angular shape were coated with nickel in the manner described in Example 1 so as to produce a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 20 to 50% nickel based on the tungsten carbide. The powder was sprayed in the manner described in Example 9, with the formation of an excellent cutting hone or lap. The sharp angular edges of the initial tungsten carbide were retained in the coating.

Similar results were obtained when using

crystalline tungsten carbide in place of the cobalt bonded tungsten carbide particles.

EXAMPLE 11

A nucleus of elemental phosphorus powder was coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 80 to 98% nickel based on the phosphorus. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying phosphorus combines with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating which has self-fluxing properties.

EXAMPLE 12

A nickel boron powder is coated with copper and the copper-coated composite further coated with nickel to form a composite-clad flame spray powder having a particle size between 100 and 325 mesh containing 63 to 67% nickel and 26 to 32% copper and 2 to 10% boron by weight. The powder is sprayed in a powder-type flame spray gun on a lightly grit-blasted steel base with the flame spray gun

and method as described in Example 1. An excellent self-fluxing alloy is formed, which when fused in place by heating with an acetylene torch, forms a dense coating which corresponds in characteristics to monel.

EXAMPLE 13

A nickel boron powder is coated with chromium and the resulting coated powder in turn coated with nickel so as to form a flame spray composite-clad powder having a mesh size between 100 and 325 and containing 70 to 80% nickel and 18 to 20% chrome and 2 to 10% boron by weight. The powder is sprayed in the manner described in Example 12, resulting in a self-fluxing alloy coating which, when fused in place in the manner described in Example 12, produces a high grade coating having characteristics similar to nichrome V.

EXAMPLE 14

Nickel-bonded titanium carbide particles having a size between 140 and 325 mesh are coated with nickel, as described in Example 1, so as to produce a nickel-clad flame spray powder having a particle size between 100 and 270 mesh and containing 20 to 50% nickel based on the titanium carbide. The material

is sprayed in the manner described in Example 1 on a base with surface roughened by grit-blasting, and a high grade, bonded titanium carbide coating is formed in which the nickel acts as a matrix binding material.

When properly finished by grinding, the resultant coating is an excellent hard-facing, extremely resistant-to-wear coating even at elevated temperatures.

Similar results are obtained when using crystalline titanium carbide particles in place of the nickel-bonded titanium carbide particles.

EXAMPLE 15

Copper powder is coated with nickel in the manner described in Example 1 so as to form a nickel-clad composite flame spray powder having a particle size between 100 and 325 mesh and containing 60 to 70% nickel based on the copper. Upon spraying in the manner described in Example 1 on a base roughened by grit-blasting or other means, an excellent, corrosion and oxidation-resistant coating is formed. A similar coating is formed if the copper is replaced with chromium in an amount of 15 to 25% chromium based on the nickel.

EXAMPLE 16

Molybdenum disilicide powder is coated with nickel in the manner described in Example 1 so as to form a composite-clad flame spray powder having a particle size between 140 mesh and 10 microns, and containing 15 to 40% nickel by weight based on the disilicide. The powder is sprayed with the flame spray gun described in Example 1 on a base material roughened by grit-blasting.

The resultant oxidation-resistant coating is very dense, but may be further improved by subsequent heat treatment in a neutral to reducing atmosphere.

EXAMPLE 17

Example 16 is repeated except in place of the nickel, nickel phosphorus is used containing 4 to 12% of phosphorus. A similar coating resulted upon spraying, which however was self-fluxing.

EXAMPLE 18

Chromium boride powder is coated with nickel in the manner described in Example 1 so as to form a flame spray powder having a mesh size between 120 and 325 and containing 15 to 50% of nickel, based on the

chromium boride. Upon spraying in the manner described in Example 1, a boride coating of high quality is obtained which is resistant to wetting by molten metals.

EXAMPLE 12

Silver solder powder is coated with nickel in the manner described in Example 1 so as to produce a nickel-clad composite powder having a size between 120 and 325 mesh and containing 25 to 50% nickel based on the silver solder. Upon spraying in the manner described in Example 1 on a base material prepared by grit-blasting, a low-fusing temperature, self-fluxing coating is formed which, when subsequently fused, is a homogenous, pore-free coating securely fused to the base material.

A simple mixture of powders consisting of 20 to 65% of this nickel-coated silver solder and 35 to 85% of a carbide (Example 10) is sprayed in the manner described in Example 1. The resultant coating, when fused, consists of angular carbide particles securely bonded to each other and to the base material.

The fused coating may be suitably finished by grinding for use as a wear-resisting coating or used, as fused, where the coated article is

to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

EXAMPLE 20

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 50% nickel based on the titanium.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the nickel and titanium combine in the flame to form a corrosion-resistant coating.

EXAMPLE 21

A niobium powder is coated with nickel in the manner described in Example 1 so as to form a composite nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 5 to 40% by weight of nickel based on the niobium.

The nickel protects the niobium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1 on a base material prepared by grit-blasting, the nickel and niobium combine in the flame to form a corrosion-resistant material.

EXAMPLE 22

A molybdenum powder was coated with nickel in the manner described in Example 1 so as to produce a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 5 to 40% nickel based on the molybdenum.

The nickel protects the molybdenum from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1 on a base material prepared by grit-blasting, the nickel and molybdenum combine in the flame to form a corrosion-resistant material.

EXAMPLE 23

A titanium boride powder was coated with nickel so as to form a flame spray powder having a particle size between 100 and 325 mesh and containing 20 to 50% nickel based on the titanium boride.

The nickel protects the titanium boride during the spray.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, a securely bonded nickel-titanium boride composite coating is achieved.

EXAMPLE 34

A silver powder is coated with nickel so as to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 30 to 70% nickel based on the silver.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the nickel and silver combine in the flame to produce a new material which is securely bonded to the base and is excellent for use as electrical contacts or the like.

During the spraying heat was evolved upon the combination of the nickel and silver, increasing the thermal economy of the process.

EXAMPLE 35

An aluminum powder is copper-plated so as to form a copper-clad flame spray powder having a particle size between 100 and 325 mesh and containing 85 to 98% or 8 to 20% copper based on the aluminum.

Upon spraying in the manner described in

Example 1, on a base material prepared by grit-blasting, the copper and aluminum combined in the flame to form a harder, corrosion-resistant alloy.

EXAMPLE 26

A silicon powder was coated with copper so as to form a copper-clad flame spray powder having a particle size between 100 and 325 mesh and containing 50 to 80% by weight of copper based on the silicon.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and silicon combine in the flame to form coatings of a material considerably more inert than copper.

EXAMPLE 27

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 50 to 80% copper based on the tellurium.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved

upon the combination of the copper and tellurium, increasing the thermal economy of the process.

[illegible]

Tin powder is coated with copper so as to form a copper-clad composite flame spray powder having a mesh size between 100 and 325 mesh and containing 75 to 95% copper based on the tin.

Upon spraying in the manner described in Example 1, upon a base material prepared by grit-blasting, the copper and tin combined in the flame to produce a ductile, corrosion-resistant coating.

[illegible]

Lead powder is coated with copper so as to form composite flame spray powder having a particle size between 100 and 325 mesh and containing 50 to 90% copper based on the lead.

Upon spraying in the manner described in Example 1, upon a base material prepared by grit-blasting, an excellent, leaded copper [illegible] is deposited which is suitable for use as a bea[illegible]

[illegible]

The nickel-clad flame spray powder of Example 1 is mixed with about 20% by weight

of low pressure polyethylene powder and [illegible] at a temperature of about 212° F. into the [illegible] of a rod of 1/8" diameter. The rod is sprayed, using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4E Gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as oxidizing gas at a pressure of 30 p.s.i. and a flow rate of 75 cu.ft./hr; with air as a blast gas at a pressure of 40 p.s.i. and a flow rate of 25 cu.ft./min. The end coating produced is similar to the coating produced in Example 1.

EXAMPLE 31

The nickel-clad flame spray powder of Example 10 is compacted and sintered in the form of a rod .125" in diameter. The rod is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. as the Metco-type 4E Gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as the oxidizing gas at a pressure of 30 p.s.i. and a flow rate of 75 cu.ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu.ft./min. The end coating produced is similar to the coating produced in Example 10.

Example 31

A wire is formed by cladding a core of aluminum in a tube of nickel and drawing to a size of .125" in diameter. The wire contains 92 to 94% by weight of nickel based on the aluminum.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4E Gun. Spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as the oxidizing gas at a pressure of 35 p.s.i. and a flow rate of 75 cu.ft./hr. Air is used as a blast gas at a pressure of 35 p.s.i. and a flow rate of 30 cu.ft./min. After initiation of the exothermic combination reaction at the melting wire tip, the flow of fuel and oxidizing gas may be drastically reduced, thus utilizing the heat of reaction to aid in melting the spray material and contributing to the over-all economy of the process. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55 - 90% by weight of nickel in the wire.

[illegible]

A coating is deposited by winding [illegible] ficial wires of nickel and aluminum and feeding the same to a [illegible] plate to obtain .002". The wire contains 5% to 10% by weight of nickel based on the aluminum. The wire is sprayed in the manner described in Example 31, with identical conditions and coating resulting.

[illegible]

A self-fluxing silver-solder powder containing 15% silver, 5% phosphorus and 80% copper, is coated with copper so as to form a composite flame spray powder having a particle size between 100 and 325 mesh and containing 20 to 50% copper based on the silver-solder.

Upon spraying in the manner described in Example 1, on a base material prepared by light grit-blasting, an excellent, low melting point, self-fluxing alloy is deposited.

[illegible]

Example 34 is repeated except nickel is used in place of the copper. Similar results are obtained.

EXAMPLE 36

A simple mixture of powders containing 10 to 25% of the composite nickel - nickel phosphorus powder described in Example 5 and 75 to 90% of copper or copper alloy powder of the kind known as "Everdur" is sprayed with the gun and spray conditions described in Example 1.

The coating as described is mechanically bonded to the base material and slightly porous by nature. It may be subsequently fused by torch or furnace heating to form a homogenous, pore-free coating welded to the base material. After fusion the coating is a fairly hard, corrosion-resistant, welded bronze overlay.

EXAMPLE 37

Example 36 is repeated, using, however, the composite nickel - phosphorus powder described in Example 11 in place of the nickel - nickel phosphorus powder.

Comparable results are obtained.

EXAMPLE 38

A simple mixture of powders containing 69% of the composite powder as described in Example 6 and 31% pure copper powder in the particle size range -140 and +325 mesh is sprayed with the gun as described in Example 1.

The coating as applied may be

subsequently fused without atmosphere control, to form a homogeneous alloy fused to the base material, which corresponds in characteristics to monel.

EXAMPLE 39

A simple mixture of powders containing 81% of the composite powder as described in Example 6 and 19% of pure chromium powder in the particle size range -140 and +325 mesh is sprayed with the gun as described in Example 1.

The coating as applied may be subsequently fused without atmosphere control, to form a homogenous alloy fused to the base material, which corresponds in characteristics to Nichrome V.

EXAMPLE 40

Example 9 is repeated except in place of the nickel, nickel phosphorus was used containing 6 to 12% of phosphorus. A similar coating resulted upon spraying, which however was self-fluxing. Fusion bonding of particles to each other and to the base was accomplished by fusing the applied coating.

EXAMPLE 41

The coated diamond powder of Example 9 is mixed with nickel-coated silver solder powder

of Example 13 in the proportion of 20 ... diamond to 35 to 80% matrix material.

The mixture was sprayed in the manner described in Example 1 and the deposit subsequently fused.

The resultant coating was a dense, pore-free coating fused to the base material in which the diamonds were securely anchored by the low melting point, self-fluxing matrix metal.

EXAMPLE 42

Example 14 is repeated except in place of the nickel, nickel phosphorus is used containing 4 to 12% of phosphorus. A similar coating resulted which, however, was self-fluxing.

EXAMPLE 43

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared

by light grit-blasting, in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

EXAMPLE 44

A molybdenum powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of

11.5 cu. ft./hr., using a No. 3 (pointed) electrode and No. 3R Argon nozzle, and using arc current of 550 amperes at 45 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 45

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 1MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder perhour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 11.5 cu. ft./hr., using a No. 3 (pointed) electrode and No. 3R Argon nozzle, and using arc current of 550 amperes at 45 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 47

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 47% zirconium and 53% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

EXAMPLE 48

A titanium powder having a particle size range between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 35% chromium and 65% titanium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the titanium base combine in the heat of the flame, forming a chromium titanium inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

EXAMPLE 49

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a

powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 11.5 cu. ft/hr., using a No. 3 (pointed) electrode and No. 3R Argon nozzle, and using arc current of 550 amperes at 45 volts.

The titanium base and silicon coating combine in the heat of the flame, forming a titanium silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 50

A dysprosium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum inter-metallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 51

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum inter-metallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 52

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in

Example 1.

The aluminum coating and the chromium base combine in the heat of the flame with a strong exothermic action, forming a chromium aluminum inter-metallic compound which deposits on the base as a dense, high quality coating of very high melting point and excellent oxidation-resistance.

EXAMPLE 53

Example 52 is repeated except that the composite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

EXAMPLE 54

The nickel-clad aluminum composite powder of Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of -140 mesh +10 microns, and preferably -140 +325 mesh in proportions of:

a) 80 weight percent tungsten carbide to 20 weight percent of the composite,

b) 20 weight percent of the carbide to 80 weight percent of the composite, and

c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface cleaned by grinding or very light sand-blast cleaning. The spraying is effected at about 8-9 inches from the plate, using a powder-type flame-spray gun as described in U.S. patent 2,961,335, issuing November 22, 1960, and sold by Metco, Inc. of Westbury, Long Island, New York under the tradename of "Thermo-Spray" powder gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 psi, and a flow rate of 20 to 30 cubic feet per hour and oxygen as the oxidizing gas at a pressure of 14 psi and a flow rate of 30 to 40 cubic feet per hour.

The nickel-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on impact with the substrate, becomes the matrix which securely binds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by proper grinding procedure, the resultant coating is of a highly wear-resistant coating material, applicable to virtually any base material and not subject to the limitations

of the previously used self-fluxing alloy matrix materials which must be fused at approximately 1900°F.

EXAMPLE 55

Example 54 is repeated except that in place of the grade of tungsten carbide cobalt powder grains used, cobalt-bonded tungsten carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 54. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resisting coating or used as deposited where the coated article is to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

EXAMPLE 56

Example 55 is repeated except that in place of the cobalt-bonded tungsten carbide grains described, the nickel-clad tungsten carbide grains described in Example 10 were substituted.

EXAMPLE 57

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 54. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means is a highly wear-resistant, hard coating.

EXAMPLE 58

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 54. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished by grinding or other means presents a highly wear-resistant, hard surface.

EXAMPLE 59

Example 54 is repeated except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium carbide, chromium carbide and mixtures of the various carbides are used.

EXAMPLE 60

The nickel-clad aluminum core composite from Example 54 is mixed with aluminum powder in the mesh size range -100 +325 mesh, and preferably in the -170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 54. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat treating in the temperature range 1250°F. to 1500°F. in reducing atmosphere, dry hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogenous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt water corrosion.

The nickel-clad aluminum composite powder of Example 54 is mixed with Monel powder of a size between -100 mesh and +440 microns, and preferably between -140 and +325 mesh in the proportions 35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 54. The resultant coating is self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, considerably increase the particle to particle bonds within the coating and decrease the permeability of the coating.

EXAMPLE 62

Example 61 is repeated except that nickel and stainless steel powders are substituted for the Monel.

EXAMPLE 63

Example 61 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished by grinding or other means shows high resistance

to abrasion, wear, and galling by other metals, and is an excellent bearing surface.

As may be noted from the foregoing the flame spraying of synergistically-acting composites in accordance with the invention is effected in the conventional manner, using the conventional flame spray equipment and utilizing conventional surface-preparation, though in certain instances wherein the spray coating has self-bonding characteristics, special surface-preparation other than a good cleaning, is not critical.

The synergistic composites in accordance with the invention may be sprayed in conjunction with or in addition to other flame-spray materials conventionally used in the art, or may be sprayed in combination with or conjunction with each other. Thus the synergistically clad powders in accordance with the invention may be sprayed in admixture with other conventional spray powders or mixtures of two or more of the composite powders in accordance with the invention. may be sprayed.

In case of powders comprised of synergistically clad particles the components of which exothermically react forming an inter-metallic compound, the spraying in admixture with other composites or with other conventional spray materials offers many advantages.

The use of these composite powders, such as nickel-coated aluminum particles, will generally improve

of the total sprayed mixture and thus of the other component or components to the substrate making the mixture self-bonding. The particle bond will also be improved so that the porosity of the coating may be decreased. The use of the composites in admixture with conventional spray powders may thus be used to improve the characteristics and properties of the materials or, conversely, the properties of the composites, such as the nickel-aluminum deposits may be enhanced or other new or better properties may be obtained.

In general as little as 20% by weight of the composits containing exothermically reacting components will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame-spray powders such as conventional metal or alloy powders. There is, of course, no upper limit on the amount as the composites may be sprayed per se, but generally about 20% by weight of the other component is required in order to have a pronounced effect on the characteristics of the coating. When, for example, using a mixture of a nickel clad aluminum powder as for instance, is shown in Example 1, with tungsten carbide, titanium carbide, tantalum carbide, chromium carbide, molybdenum, niobium and tantalum amounts of 20% to 80%, and preferably 25% to 50% by weight of the composite may be used. The mixtures are self-bonding as sprayed and form abrasion and wear-resistant coatings. When the same composite is sprayed in mixture with Monel, stainless steel, nickel, chromium, etc., amounts of 25% to 75% by weight of the composite, and

preferably 30% to 40% by weight of the composite are used. When sprayed in admixture with aluminum as little as 5% of the aluminum will vary the characteristics of the coating, though preferably up to 25% of the aluminum is used. The composite as mentioned may also be sprayed in admixture with iron, nickel or nichrome or produce a self-bonding mixture which produces a coating of lower permeability. It is of course, impractical to list all of the materials which may be sprayed in conjunction or admixture with the composites in accordance with the invention, but the selection of such materials for specific purposes is within the skill of the artisan in light of the disclosure.

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention is therefore only intended to be limited by the appended claims or their equivalents wherein we have endeavored to claim all inherent novelty.

~~This application is a continuation-in-part of our copending application Serial No. 72 543, filed November 22, 1960.~~

We claim:

1. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of individual, synergistically clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and synergistically acting with the said nucleus in the process.

2. Improvement according to claim 1 in which said nucleus and said coating layer are of materials exothermically reacting with each other at the temperature developed in said heating zone.

3. Improvement according to claim 1 in which said coating layer comprises a bonding agent for said nucleus.

4. Improvement according to claim 1 in which said nucleus contains a self-fluxing material.

5. Improvement according to claim 1 in which said nucleus comprises a refractory material and in which said coating comprises a bonding matrix for said nucleus.

6. Improvement according to claim 1 in which said coating layer comprises nickel and in which said nucleus is a member selected from the group consisting of aluminum, nickel-phosphorus, nickel-boron, phosphorus-copper, chromium, silver solder, and silver.

7. Improvement according to claim 6 in which said coating material is nickel and in which said nucleus contains aluminum, said aluminum being present in amounts of about 10 to 45% based on the nickel.

8. Improvement according to claim 1 in which said coating layer is nickel and said nucleus a refractory material.

9. Improvement according to claim 1 in which said coating layer is nickel and said nucleus is a carbide.

10. Improvement according to claim 9 in which said carbide is tungsten carbide.

11. Improvement according to claim 1 in which said coating layer is nickel and in which said nucleus is aluminum oxide.

12. Improvement according to claim 1 in which said coating layer is nickel and said nucleus is diamond.

13. Improvement according to claim 1 in which said coating layer is nickel and said nucleus is aluminum, and in which said [illegible] are passed into said [illegible] refractory oxide [illegible].

14. Improvement according to claim 13 in which said refractory oxide is aluminum oxide.

15. Improvement according to claim 1 in which said coating layer is cobalt and said nucleus is chrom[illegible].

16. Improvement according to claim 1 in which said coating layer is copper and in which said nucleus comprises a member selected from the group consisting of tin, lead, and aluminum.

17. Improvement according to claim 1 in which one of said coating layer and said nucleus comprises silicon and the other a member selected from the group consisting of molybdenum, chromium, aluminum and titanium.

18. Improvement according to claim 1 in which one of said coating layer and said nucleus comprises chromium and the other a member selected from the group consisting of silicon, zirconium, titanium and aluminum.

19. Improvement according to claim 1 in which one of said coating layer and said nucleus comprises aluminum and the other a member selected from the group consisting of dysprosium, lanthanum and chromium.

20. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite comprising at least two exothermically reacting components.

21. Improvement according to claim 20 in which said heat-fusible material is in the form of a wire.

22. Improvement according to claim 21 in which one component of said composite comprises nickel and the other aluminum.

23. Improvement according to claim 22 in which said wire has an aluminum core and nickel covering.

24. A flame spray powder in the form of individual, synergistically clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus ~~and synergistically active with said nucleus in flame spraying~~.

25. A flame spray powder according to claim 24 in which said nucleus and said coating layer are of exothermically reacting materials.

26. A flame spray powder according to claim 24 in which said coating layer comprises a bonding agent for said nucleus.

27. A flame spray powder according to claim 24 in which said nucleus contains a self-fluxing material.

28. 2. A flame spray powder according to claim 24 in which said nucleus comprises a refractory material and said coating comprises a bonding matrix for the material of said nucleus.

29. A flame spray powder according to claim 24 in which said coating layer comprises nickel and in which said nucleus is a member selected from the group consisting of aluminum, nickel-phosphorus, nickel-boron, phosphorus-copper, chromium, silver solder, and silver.

30. A flame spray powder according to claim 24 in which said coating material is nickel and in which said nucleus contains aluminum, said aluminum being present in amounts of about 10 to 45% based on the nickel.

~~31.~~ 3. A flame spray powder according to claim ~~24~~ 1 in which said coating layer is nickel and said nucleus is a refractory material.

~~32.~~ 4. A flame spray powder according to claim ~~24~~ 1 in which said coating layer is nickel and said nucleus is a carbide.

~~33.~~ 5. A flame spray powder according to claim ~~32~~ 4 in which said carbide is tungsten carbide.

~~34.~~ 6. A flame spray powder according to claim ~~24~~ 1 in which said coating layer is nickel and said nucleus is aluminum oxide.

~~35.~~ 7. A flame spray powder according to claim ~~24~~ 1 in which said coating layer is nickel and said nucleus is diamond.

---

36. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus contains aluminum, and in which said powder is in admixture with a refractory oxide powder.

37. A flame spray powder according to claim ~~24~~ 36 in which said refractory oxide powder is aluminum oxide powder.

38. A flame spray powder according to claim ~~24~~ 36 in which said ~~coating layer is cobalt and said nucleus is~~ refractory oxide powder is zirconia.

39. A flame spray powder according to claim 24 in which said coating layer is copper and said nucleus comprises a member selected from the group consisting of tin, lead and aluminum.

~~40.~~ 8. A flame spray powder according to claim ~~24~~ 1 in which said powder is bonded in the form of a wire.

41. A flame spray powder according to claim 24 in which one of said coating layer and said nucleus comprises silicon and the other a member selected from the group consisting of molybdenum, chromium, aluminum and titanium.

42. A flame spray powder according to claim 24 in which one of said coating layer and said nucleus comprises chromium and the other a member selected from the group consisting of silicon, zirconium, titanium and aluminum.

43. A flame spray powder according to claim 24 in which one of said coating layer and said nucleus comprises aluminum and the other a member selected from the group consisting of dysprosium, lanthanum and chromium.

~~44.~~ 9. A flame spray powder according to claim ~~24~~ 1 including at least one additional coating layer differing from said nucleus and first mentioned coating layer and synergistically active with at least one of said nucleus and first mentioned coating layer in flame spraying.

45. A flame spray material in the form of a composite comprising at least two exothermically reacting components in intimate contact with each other.

46. A flame spray wire containing at least two exothermically reacting components in intimate contact with each other.

47. A flame spray wire according to claim 46 in which one of said components comprises nickel and the other aluminum.

48. A flame spray wire according to claim 47 in which said wire has an aluminum core and nickel covering.

49. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of individual, synergistically clad particles comprising a nucleus and at least two coating layers of materials differing from each other and synergistically acting with each other in the process.

50. A flame spray powder in the form of individual, synergistically clad particles comprising a nucleus and at least two separate coating layers of material differing from each other and synergistically active with each other in flame spraying.

51. In the flame spraying process in which a heat-fusible material is sprayed onto a base, the improvement to increase the bond which comprises spraying an intermediate layer of two components exothermically reacting with each other, forming an inter-metallic compound.

52. Improvement according to claim 51 in which one of said components comprises nickel and the other aluminum.

53. Improvement according to claim 51 in which one of said components comprises chromium and the other aluminum.

54. A base having a flame spray coating bonded in place by an intermediate bonding layer of an inter-metallic compound formed from two exothermically reacting components.

55. An article according to claim 54 in which said inter-metallic compound is a nickel aluminum inter-metallic compound.

56. An article according to claim 54 in which said inter-metallic compound is a chromium aluminum inter-metallic compound.

57. A base having a flame sprayed coating of an inter-metallic compound formed of two exothermically reacting components.

58. A coated base according to claim 57 in which said inter-metallic compound is a nickel aluminum inter-metallic compound.

59. A coated base according to claim 57 in which said inter-metallic compound is a chromium aluminum inter-metallic compound.

60. A base having a flame sprayed coating produced by the process according to claim 1.

61. A base having a flame sprayed coating produced by the process according to claim 49.

62. Improvement according to claim 6 in which said coating material is nickel and in which said nucleus contains aluminum, said aluminum being present in amounts of about 16 to 18% based on the nickel.

63. Improvement according to claim 1 in which said synergistically clad particles are passed into said heating zone in admixture with another heat-fusible material.

64. Improvement according to claim 63 in which said nucleus and said coating layer are of materials exothermically reacting with each other at the temperature developed in said heating zone forming an inter-metallic compound.

65. Improvement according to claim 64 in which said coating material is nickel and in which said nucleus contains aluminum, said aluminum being present in amounts of about 10 to 45% based on the nickel.

66. Flame spray powder according to claim 65 in which said nucleus and said coating layer are of materials which will exothermically react when heated to form an inter-metallic compound and in which said powder is in admixture with another flame spray powder.

67. Flame spray powder according to claim 66 in which said coating material is nickel and in which said nucleus contains aluminum in amounts of about 10 to 40% based on the nickel.

Add C²

E 307

OATH, POWER OF ATTORNEY AND PETITION

Being duly sworn, we, Ferdinand J. Dittrich and Arthur P. Shepard, residing at 2457 New Place, Bellmore, Long Island, New York and 29-01 - 159th Street Flushing, Long Island, New York, respectively, depose and say that we are citizens of the United States; that we have read the foregoing specification and claims and we verily believe that we are the original, first and joint inventors of the invention or discovery of FLAME SPRAYING SYNERGISTIC COMPOSITES described therein; that this application discloses and claims subject matter disclosed in our pending application U. S. Serial No. 72,543, filed November 22,1960 that as to the subject matter of this application which is common to said application we do not know and do not believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than one year prior to said application, or in public use or on sale in the United States for more than one year prior to said application; that said common subject matter has not been patented before the date of said application in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months prior to said application; that as to the subject matter of this application which is not common to said application we do not know and do not believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than

one year prior to this application or in public use or on sale in the United States for more than one year prior to this application, and that said subject matter has not been patented in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months prior to this application; and that no application for patent on said invention has been filed by us or our representatives or assigns in any country foreign to the United States.

And we hereby appoint BURGESS, DINKLAGE & SPRUNG (Registration No. 15,379), a firm composed of Ralph D. Dinklage and Arnold Sprung, of 233 Broadway, New York 7, New York our attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith.

WHEREFORE, we pray that letters Patent be granted to us for the invention or discovery described and claimed in the foregoing specification and claims, and we hereby subscribe our names to the foregoing specification and claims, oath, power of attorney, and this petition, this 7th day of June, 1961.

Inventor: Ferdinand J. Dittrich
2457 New Place, Bellmore, Long Island, New York

Inventor: Arthur P. Shepard
29-01 159th Street, Flushing, Long Island, N. Y.

State of New York
County of Nassau } SS.

Before me personally appeared Ferdinand J. Dittrich and Arthur P. Shepard, to me known to be the persons described

In the above application for patent, [illegible] foregoing instrument is my product, and made oath before me to the allegations set forth therein as being under oath, on the day and year aforesaid.

_____

[illegible] New York

[illegible] County

1/29/183.5 29-183.5 7 June 66 134544 3254970 Div. 4 110 #2

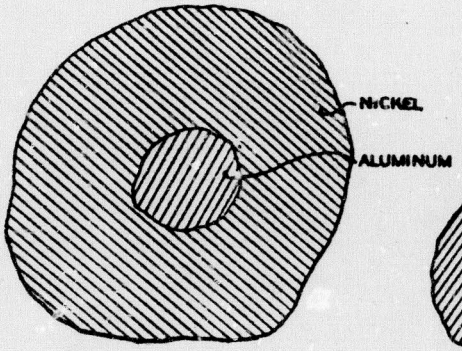

Fig. 1

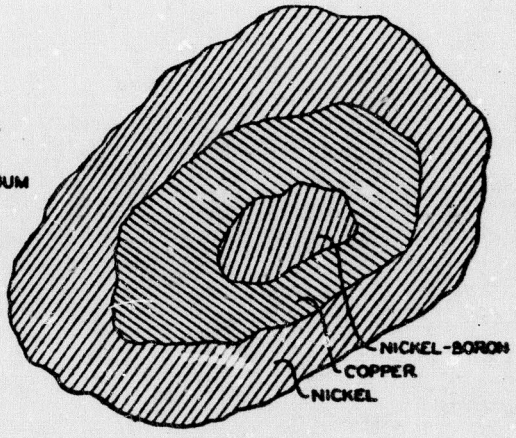

Fig. 2

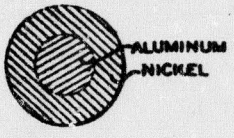

Fig. 3

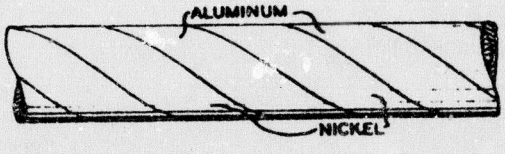

Fig. 4

INVENTORS
FERDINAND J. DITTRICH
ARTHUR P. SHEPARD
BY
Burgess Dinklage & Sprung
ATTORNEYS

M305

E 311

SEP 13 1962

Bd. 22

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 134,544 Div. 2

Filed : August 30, 1961

For : FLAME SPRAYING SYNTHETIC COMPOSITES

September 10, 1962

Hon. Commissioner of Patents
Washington 25, D. C.

Sir:

The following is an amendment offered before the first Office Action. Kindly enter the following amendment:

Claim 27, line 1, change "24" to --30--

Claim 38, line 1, change "24" to --30--, cancel lines 2 and 3 and substitute --which said refractory oxide powder is zirconia powder --.

REMARKS

The above amendment has been offered to amend the claims to cover specific preferred embodiments of the invention as set forth in Examples 3 and 4.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By _____
Attorneys for Applicant

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 312

PAPER No. 3

Burgess, Dinklage & Sprung
233 Broadway
New York 7, N.Y.

Applicant: Ferdinand J. Dittrich et al
Ser. No. 134,544
Filed August 16, 1961
For FLAME SPRAYING SYNERGISTIC COMPOSITES

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

This application has been examined.

References cited to show classification:

I.	Wasserman	2,288,869	July 7, 1942	117-46
	Gutzeit	2,908,589	Oct. 13, 1959	117-46
II.	Robinson	2,612,581	Sept. 30, 1952	29-191
	Homer et al	2,933,415	Apr. 19, 1960	29-191

This application is found to contain claims drawn to two separate and distinct inventions. Restriction as indicated below is required under Rule 142.

I. Claims 1-23, 49, and 51-65, drawn to a process of flame spraying and a flame-sprayed article, would be classified in class 117, subclass 46, as indicated by the patents to Wasserman and Gutzeit et al, and

II. Claims 24-48, 50, 66, and 67, drawn to composite metal stock, would be classified in class 29, subclass 191, as indicated by the patents to Robinson and Homer et al.

The two inventions are distinct from the other, because the composite wire and powder of the claims of Group II have utility other than in the flame spraying process

defined in the claims of Group I. For example, the composite metal powder of the claims of Group II could be used in the fabrication of metal parts from the compressed compacted powder, as shown by the Homer et al patent, and the composite metal wire could be used as a welding rod, as shown by the Johnson patent.

Since these distinct inventions have acquired a separate status in the art by the issuance of patents to such individual patentee as shown by the above cited exemplary art, restriction for examination purposes indicated is proper.

Applicants are advised that their response to be complete must include a provisional election of one of the above inventions identified as I or II. (see Rule 143), even though they traverse the requirement.

Summary:

Claims subject to restriction: 1-67.

Claims rejected: None.

Claims allowed: None.

rel

W. F. Sullivan/les

L. Martin
Examiner

Metco 305.1
AS/k

E 314

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 134 544 Div. (25

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

November 23, 1962

Hon. Commissioner of Patents
Washington 25, D. C.

Sir:

The following is in response to the Office Action dated September 19, 1962.

Kindly cancel claims 1 to 23, 49, and 51-65 without prejudice.

REMARKS

In accordance with the requirement for restriction claims 24-48, 50, 66 and 67 directed to Invention II are hereby elected for further prosecution. The non-elected claims of Group I have been cancelled and made the subject matter of a divisional application in accordance with Rule 147.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

Paper No. 6

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 315

In Reply Please Refer To:

Burgess, Dinklage and Sprung
233 Broadway
New York 7, New York

Applicant: Ferdinand J. Dittrich et al.
Ser. No. 134,544
Filed Aug. 16, 1961
For FLAME SPRAYING SYNERGISTIC COMPOSITES

MAILED
JAN 3 1964
GROUP 110

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

This application has been examined.

References applied:

Harshaw	1,986,197	Jan. 1, 1935	75-0.55
Wulff	2,359,401	Oct. 3, 1944	75-0.55
Poorman et al.	2,714,563	Aug. 2, 1955	29-194
Shepard	2,936,229	May 10, 1960	75-0.55

Claims 24-28, 40, 44-48, 50, and 66 are rejected as failing to particularly point out and distinctly claim the invention as required in 35 U.S.C. 112. The claims are too broad because they do not recite the materials that will produce the desired result. Furthermore they are functional wherein they recite the materials in terms of the result desired rather than a positive recitation as to the materials themselves.

Claims 24-48, 50, and 66 and 67 are rejected as unpatentable over Shepard and Wulff, each applied individually in view of Harshaw and Poorman et al. The basic references disclose flame spray powders containing elements that read on the claimed subject matter except for the clad particles that have a nucleus and a coating layer of another material which is disclosed by Harshaw

and the fact that it is old and well known in the art to use refractory powders (Poorman et al.) in flame spraying. Therefore in view of the above cited prior art no invention is seen in the claimed matter because the applicants' are only doing that which the prior art teaches.

No claim is allowed.

H. Bizot
Examiner

ROD

RODean:cjg

E 317

RECEIVED

JUL - 7 1964

GROUP 110

Applicants : [illegible]

Serial No. : 134,[illegible]

Filed : [illegible]

For : [illegible]
COMPOSITIONS

July 1, 1964

Hon. Commissioner of Patents
Washington, D.C. 20231

Sir:

The following is in response to the Office Action dated January [illegible], 1964. Kindly [illegible] following amendment:

In Claim 24, cancel [illegible] on line 4, through "spraying" on line 5, and [illegible] following:

, one of said [illegible] consisting essentially of a refractory material, [illegible] for said refractory material.

Cancel claims 25 through 27, 29, 30, 36 through 38, 41 through 43, 45 through [illegible], 50, 65 and 67 without prejudice and substitute the following therefor:

10. The [illegible] according to claim 24 in which said refractory material is a refractory oxide.

11. The [illegible] according to claim 10 in which said refractory oxide is a member selected from the group consisting of alumina and silica.

12. Claim [illegible] which [illegible] is a refractory carbide.

12 Claim [illegible] according to claim 12 in which said refractory carbide is tungsten carbide.

14 Claim [illegible] according to claim [illegible] in which said refractory material is diamond.

REMARKS

The claims may be limited to the embodiment of the application in which the composite [illegible] may contain [illegible] powder particles, with one of the [illegible] metal melting comprising a refractory material and the other a bonding matrix for this refractory material. This embodiment is generically disclosed, for example, on page 7, second full paragraph, and there are numerous examples thereof. It is furthermore believed that the limitation of the claims to the specific materials has overcome the Examiner's formal objection to the former claims as being too broad because they do not recite the materials that will produce the desired result.

Claim [illegible] powder is

the form of [illegible] a nucleus of the refractory material, such as, for example, oxide, carbide, or [illegible], and a coating material in the form of a bonding matrix for the refractory material, is entirely novel and is [illegible] taught nor indicated by any of the cited references.

The Harshaw patent teaches a metallic composition consisting of metal particles with a metal coating which is used for compacting and heating into a body to form an alloy of the two metals. There is not the remotest teaching or indication of a clad flame spray powder, let alone a powder having a refractory material as one of the components, such as the nucleus and a bonding matrix for this as the coating layer.

The Gilfillan patent [illegible] to teaching a clad flame spray powder [illegible] of metals.

The Shepard patent discloses a spraywelding alloy powder which [illegible] relation or similarity to a clad powder as claimed herein.

The Poorman et al. patent discloses the spraying of refractory materials but has no disclosure or teaching relating to clad powder particles.

The [illegible] individual powder particles containing a nucleus and a coating layer, one of which is a refractory material and the other a bonding matrix therefor, is entirely novel to the applicants and produces superior spraying results and superior coatings in which the refractory is bonded to [illegible] completely and securely. From

Marshaw's [illegible] alloy powder [illegible] under [illegible] alloy body, [illegible] of spray [illegible] matrix therefor.

In view of the [illegible], reconsideration and allowance of the claims as amended, is hereby solicited.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

BY

Attorneys for Applicants

60-17

E 321

IN THE UNITED STATES PATENT OFFICE

RECEIVED

JUL - 8 1964

Applicant : Ferdinand J. Dietrich et al.

Serial No.: 134,546

Filed : Aug. 14, 1961

For : FLAME SPRAYED SYNTHETIC RESIN COMPOSITES

Group 110

July 2, 1964

Hon. Commissioner of Patents
Washington 25, D.C.

Sir:

BURGESS, DINKLAGE & SPRUNG, attorneys of record in the above entitled application, announce their change of address as of April 30, 1964 to 605 Third Avenue, New York City, N.Y. 10016, and respectfully request that all future correspondence and actions be addressed to them at that address.

BURGESS, DINKLAGE & SPRUNG

BY Arnold Sprung

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 322

IN REPLY PLEASE REFER TO:

Burgess, Dinklage and Sprung
605 Third Avenue
New York City, New York 10016

Applicant: Ferdinand J. Dittrich et al.	
Ser. No. 134,544	MAILED
Filed Aug. 16, 1961	JUL 24 1964
For FLAME SPRAYING SYNERGISTIC COMPOSITES	GROUP [illegible]

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

SHORTENED TIME FOR REPLY

Responsive to the amendment filed July 2, 1964.

Additional references:

Alexander et al.	2,949,358 (Filed Sept. 23, 1957)	Aug. 16, 1960	75-176
Wheildon	3,006,782 (Filed Mar. 9, 1956)	Oct. 31, 1961	29-195
Dawson	3,023,490 (Filed Nov. 25, 1955)	Mar. 6, 1962	29-195

Claims 24, 28, 31-35, 40, 44 and 68-72 are rejected for failing to particularly point out and distinctly claim the invention as required in 35 U.S.C. 112. The use of the words "refractory material", "bonding matrix", "refractory oxide", etc make the claims too broad because they cover materials that will not produce the desired result. Furthermore, they are indefinite because it is not understood just what the words mean.

Claims 24, 28, 31-35, 40, 44 and 68-72 are rejected as unpatentable over Dawson and Alexander et al, each applied individually in view of Wheildon and Poorman et al. The basic references disclose clad powders in which

the nucleus comprises a refractory material and the coating comprises a bonding matrix for the material of said nucleus. Note particularly Alexander et al page 1, column 2, lines 39-41. Wheildon discloses that it is old to use refractory oxides in flame spraying. Poorman et al discloses that it is old to use refractory powders in flame spraying. Therefore in view of the secondary references it would not be invention to use the powders of the basic references in flame spraying because that is what the prior art teaches. No invention is seen in the claimed subject matter.

No claim allowed.

This is a FINAL REJECTION.

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE FOUR MONTHS FROM THE DATE OF THIS LETTER.

D.L. Reck
Examiner

ROD

RODean/mlh

Wo.7-2503

Metco 305.1
AS:jl

E 324 SEP -3

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al.

Serial No. : 134,544 Group 116

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

August 27, 1964

Hon. Commissioner of Patents

Washington 25, D.C.

Sir:

The following is in response to the Office Action dated July 24, 1964. Kindly enter the following amendment:

Claim 24, line 2, after "particles", insert -- of a size between about 60 mesh and plus 3 microns --

lines 4, and 5, cancel the amendment thereto and substitute the following: -- one of said coating layer and nucleus comprising a refractory selected from the group consisting of refractory oxides, refractory carbides, and diamond, the other a bonding matrix for said refractory material selected from the group consisting of nickel and cobalt matrices --

REMARKS

It is well known to flame spray refractory materials, such as refractory oxides and carbides and to provide a bonding matrix for the sprayed material. The spray material for this purpose was conventionally in

the form of individual particles of the matrix bonded refractories or mixtures of particles of the refractories and the binding matrix.

The Applicants' invention as now claimed is directed to a flame spray powder in which the individual powder particles are in the form of a nucleus provided with a coating layer, the nucleus and coating layer forming the separate constituents, i.e. the refractory material and the matrix.

By providing the flame spray powder in this novel form in which, for example, the matrix forms a separate and distinct coating layer on the nucleus of the refractory particles substantially improved results are obtained in the flame spraying allowing the production of superior, more uniform coatings with higher deposit efficiencies. None of the references cited by the Examiner teaches nor indicates the concept of providing the matrix as a separate and distinct coating layer on a nucleus of the refractory material in a flame spray powder.

The newly cited Alexander et al patent relates to a refractory metal alloy and not to a flame spray powder. The Alexander et al metal alloy is molybdenum, rhenium, or tungsten which has very fine, submicron refractory particles dispersed throughout. In accordance with one mode of

producing this reinforced alloy, the submicron refractory oxide particles are coated with the metal, i.e. the molybdenum, rhenium, and tungsten, and then further processed to form the metal body. Even, however, at this intermediate stage of production, the coated particles do not constitute a coated flame spray powder as claimed by the Applicants or the equivalent thereof.

In the first place, the coating layer is molybdenum, rhenium, or tungsten and is thus obviously not a bonding matrix. In order to further distinguish from the reference, the bonding matrix in accordance with the Applicants' claims has been limited to nickel and cobalt matrices.

In the second place, the powder is much too fine to constitute a flame spray powder as it has a submicron size in the millimicron range. As is well known in the art flame sprayed powder must be substantially larger and the size limitation has been inserted in the claims.

The Dawson patent, newly cited, simply discloses an armored coating of a matrix containing hard refractory particles. The Applicants do not claim that such a coating is novel. The claimed novelty in the particular form of the flame spray powder from which such a coating is deposited by the flame spray process. There is nothing in Dawson to indicate nor teach the initial powder in this form, and it may be noted that wherein a powder mixture is applied, this is a true mixture of the matrix and the refractory particles (see col. 6, lines 28-31).

Wheildon, newly cited, and Poorman et al of record have merely been cited to show that it is old

old to use refractory powders in flame spraying. This is readily admitted by the Applicants and the invention is not directed to the use of such refractory powders in flame spraying but resides in a particular novel form of the powders for this purpose, i.e. as coated powders. Such coated powders are nowhere disclosed in Wheildon or Poorman et al, and it should be further noted that Poorman actually does not relate to flame spraying as the term is conventionally used in the art but relates to a special detonation high velocity deposition process.

It is thus believed clear that none of the cited art teaches the Applicants' flame sprayed powder having the improved form of the coated particles.

In order to overcome the Examiner's formal objections to the claims, the refractory material has been limited to refractory oxides, carbides, and diamond. It should be noted from the art cited by the Examiner himself that it is conventional to generically refer to the material as refractory. Further, the invention does not reside in the particular refractory oxides or carbides, but the use of these conventional materials in the particular particle form.

The bonding matrix has furthermore been limited to nickel and cobalt.

In view of the above favorable consideration and allowance of the claims is respectfully solicited.

If, however, the Examiner does not consider the above as placing

application in condition for allowance, it is respectfully requested that the Examiner telephone the undersigned attorneys at 212-MO-1-520 for a conference in accordance with the Commissioner's Directive.

Respectfully submitted,

BURGESS, DINKLAGE, & SPRUNG

By: _____
Attorneys for the Applicants

Paper No. 11

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 329

In Reply Please Refer To:

Burgess, Dinklage and Sprung
605 Third Avenue
New York City, New York 10016

Applicant: Ferdinand J. Dittrich et al.

Ser. No. 134,544

Filed Aug. 16, 1961

For FLAME SPRAYING SYNERGISTIC COMPOSITES

MAILED

SEP 14 1964

GROUP 1

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

Responsive to the amendment filed August 31, 1964.

The amendment filed August 31, 1964 has been entered. The claims as amended have been considered along with applicants' argument with respect to the foregoing claims. The claims are, however, upon review still considered to be unpatentable over the references and for the reasons set forth in the final rejection.

The request for a telephone call has been noted but has not been complied with for the reasons that it appeared to the examiner that the requested telephone interview would not be effective to advance the prosecution of the case.

No claim allowed.

The statutory time limit runs from the date of the final rejection.

Earl T. Rick
Examiner

ROD

RODean/mlh

OCT 15 1964

E 330

Metco 305.1
AS/k

OCT 19 1964

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 134 544 Group 110

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

October 14, 1964

Hon. Commissioner of Patents
Washington, D. C.

Sir:

The following is in further response to the Office Action dated July 24, 1964 and the Action dated September 14, 1964.

REMARKS

Enclosed for the record are affidavits of Dr. H. Ingham, Jr., Frank Nicholas Longo, Arthur P. Shepard and F. J. Dittrich. These affidavits were not and could not be presented before final rejection as the art and issues to which the same are directed were cited and raised for the first time in the final rejection of July 24, 1964.

It is believed that the affidavits conclusively show an unexpected superiority for the coated flame spray powders claimed in the instant application and for the process of flame spraying the same. The affidavits show a surprising and unexpected increase in deposit efficiency when spraying these coated or clad particles as compared to an aggregate

(the conventional matrix [illegible], a mixture of refractory and [illegible], not clad, powder per se, as shown in the Dawson, Wa[illegible] and Domanski et al references. The affidavits further show that sub-micron size particles disclosed by Alexander et al could not be used for flame spraying, or be considered a flame spray powder, even if of the claimed composition. Actually, the Alexander et al sub-micron particles are not refractory oxides coated with a nickel or cobalt matrix material, but are sub-micron oxide particles coated with a metal such as molybdenum as an intermediate in the production of a metal composition, which has nothing to do with flame spraying or the invention.

Dawson does not disclose a powder consisting of the clad particles and which teaches the conventional matrix bonded refractory [illegible] in the form of an agglomerate and not individual clad particles consisting of a nucleus and coating layer. As conclusively shown in the affidavits, the applicants' clad flame spray powders would not be obvious and it would not be obvious that the same would produce superior results in flame spraying. In the prior art there were a number of problems encountered in spraying refractory particles, such as refractory carbides and oxides. It was extremely difficult to obtain a dense, adherent, satisfactory coating of refractory carbides per se, unless a bonding matrix was provided. If such bonding matrix were used in the conventional form [illegible] the matrix bonding is rather and contains [illegible] carbide, the

coating only to obtain with a relatively low deposit efficiency, resulting in a loss of the grit. Furthermore, the coatings were not as uniform as could be desired and it was not possible to obtain sharp, angular hard particles in the coating which were best used for abrasive purposes. If it were attempted to spray a mixture of the refractory carbide or oxide and the matrix, an extremely low deposit efficiency would occur for the refractory with a relatively higher deposit efficiency for the matrix, so that in effect a coating of the matrix containing uneven and substantially lower amounts of the refractory were formed.

Very surprisingly and unexpectedly, with the use of the clad particles in accordance with the invention, a relatively high deposit efficiency is achieved and an extremely uniform adherent coating formed. It is possible in accordance with the invention to flame-spray coatings containing angular, sharp, hard refractory particles for abrasive purposes and to flame-spray materials, such as tungsten carbide which has a strong tendency to decarburize, or otherwise deteriorate when flame-sprayed. It is furthermore possible to spray materials which could not be sprayed per se, as they would not be heat-softened, as for example, diamonds.

In view of the above and the affidavits, reconsideration and allowance of the claims is hereby solicited.

Respectfully submitted,

[illegible], WILLIAMS & SPRUNG

By [illegible]
Attorneys for Applicants

E 333 Metco 305.1
JS/k

OCT 19 1964

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 134 544 Group 110

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

AFFIDAVIT

STATE OF NEW YORK)
) SS:
COUNTY OF NASSAU)

HERBERT S. INGHAM, JR. being duly sworn deposes and says that he is Manager of the Research and Development Department of Metco, Inc. of Westbury, Long Island, New York. Deponent has received the Bachelor's degree in Physics from the Rensselaer Polytechnic Institute in 1953, his Master's degree in Physics from the Carnegie Institute of Technology in 1956, and his Ph.D. from this Institute in 1959.

As Manager of the Research and Development Department of Metco Inc., deponent is fully familiar with all phases of flame spraying, including powder flame spraying. In order to be considered a flame spray powder, the powder must have a particle size which is predominantly above at least 5 microns and powders which have a particle size below this, or contain a substantial portion of particles having such a smaller size may not be considered flame spray particles and could not be satisfactorily flame sprayed. Deponent is familiar with all commercial powder flame spray guns and equipment available, and knows of no equipment that could handle a spray powder

of a size below 5 microns. Deponent's experience in attempting to spray fine powders has shown that the same are not free flowing, cannot be satisfactorily fed through the flame spray gun, and if actually passed through the gun will oxidize excessively, or will ignite or volatilize, will stick to and load the nozzle, or will carry with the gas stream and not even strike substrate, and cannot form satisfactory coatings. Deponent has studied U.S. patent No. 2 949 358 of August 16, 1960 to Alexander et al and states that the powder described on page 1, column 2, lines 39-41 in view of column 1, lines 20-23, which is used in the production of the patentee's alloys, may not be considered a flame spray powder and could not be sprayed. These particles have a particle size within the millimicron range and thus cannot possibly be flame sprayed.

Further deponent sayeth not.

Herbert S. Ingham, Jr.

Subscribed and sworn to before me this __day of _____, 1964

_____

OCT 19 1964 AS/k

E 335

Part B Paper #1

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 134 544 Group 110

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

AFFIDAVIT

STATE OF NEW YORK)
) SS:
COUNTY OF NASSAU)

FRANK NICHOLAS LONGO being duly sworn deposes and says:

Deponent is a metallurgical engineer having received his degree from the Polytechnic Institute of Brooklyn, New York, and is employed as a project engineer with the Research and Development Department of Metco Inc., Westbury, Long Island, N.Y. In his position as project engineer deponent is fully familiar with the flame spray field and has primary responsibility for the development of powders for flame spraying and for the analysis of flame spray coatings.

The following experiments were conducted by deponent:

Experiment 1

3 batches of powder containing 6% by weight of a matrix material and the remainder tungsten carbide were made up with each of the batches being identical except for its physical form. The first batch consisting of cobalt matrix bonded tungsten carbide particles (the cobalt acting as the

matrix), the second batch consisting of tungsten carbide particles coated with the nickel in accordance with U.S. patent application Serial No. 134 544 of August 16, 1961, and the third batch consisting of a mixture of nickel particles and tungsten carbide particles. The particles of the first batch were in the form of conventional aggregate of sub-particles of tungsten carbide bonded together by the cobalt matrix. The second batch was formed in the manner described in U.S. patent application 134 544 by cladding the tungsten carbide particles with nickel.

Each of the batches was carefully screened to the same size range between minus 200 and plus 270 mesh and each batch was sprayed in the identical manner on a mild steel substrate prepared by rough grit blasting using a Metco THERMOSPRAY gun with acetylene at 10 PSIG and 25 SCFH, and oxygen at 12 lbs. PSIG and 35 SCFH. Spraying was effected at a distance of 7" using 6-7 pounds per hour. The deposit efficiency (% of particles sprayed adhering to the base) was measured in the conventional manner. The deposit efficiency of the first batch sprayed was 21%, the second batch 50%, and the third batch 10%. The coating produced with the first and second batch was a coherent carbide containing porous coating, while the coating obtained with the third batch was essentially a nickel coating containing very little carbide.

Experiment 2

Experiment 1 was repeated, however, only spraying batch 2 in which the nickel content was reduced to 2-1/2%. The deposit efficiency was 40%.

In Experiment 1 deponent used cobalt as the matrix for the first batch of powder, and nickel as the matrix for the second batch of powder as the cobalt matrix bonded tungsten carbide was the only matrix bonded tungsten carbide readily available to deponent at the time the experiments were run, and the nickel coated tungsten carbide was the only readily available coated tungsten carbide at the time the experiments were run. Nickel and cobalt are however, equivalents as matrixes for binding carbides and deponent knows from his own experience that no significant differences in the experiment could occur by substituting the cobalt with nickel in batch 1, or the nickel with cobalt in batch 2.

CONCLUSION

The use of a clad, or coated refractory powder as described in application Serial No. 134 544 allows flame-spraying with a substantially higher deposit efficiency than could be achieved with corresponding refractory aggregates generally referred to in the art as matrix-bonded refractory powders. Mere mixtures of the refractory particles and particles of the bonding matrix cannot produce satisfactory refractory coatings.

Further deponent sayeth not.

Frank Nicholas Longo

Frank Nicholas Longo

Subscribed and sworn to before me this ___ day of _____, 1964

E 338

Part B, Paper #1

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 134 544 Group 110

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

AFFIDAVIT

STATE OF NEW YORK)
) SS:
COUNTY OF NASSAU)

FERDINAND J. DITTRICH being duly sworn deposes and says:

Deponent is Senior Engineer in the Research and Development Department of Metco Inc. of Westbury, Long Island, New York, and has had over 25 years experience in the flame spray field. Deponent is a member of the American Society for Metals, Society for Aerospace Material and Process Engineers, and the American Powder Metallurgy Institute, and has presented papers on original work at national meetings of the American Ceramic Society and the Society of Aerospace Materials and Process Engineers. Deponent is the inventor of a number of patents relating to the flame spray field. Deponent is one of the inventors named in the above entitled application and is familiar with the subject matter of the application and the art cited by the Examiner in support of the final rejection.

The following test was conducted by deponent:

Two batches of flame spray powder were made up each having the same particle size between minus 270 mesh and plus 10 microns. The first batch consisted of zirconium oxide powder the particles of which were coated with 40% by weight of cobalt in accordance with the above entitled application. The second batch consisted of a mixture of zirconium oxide powder with 40% by weight of cobalt powder. Each of these batches was sprayed under identical conditions onto a mild steel substrate prepared by rough grit blasting. The spraying was effected with the Metco 2 MB plasma flame spraygun using an E nozzle, with nitrogen as the primary plasma gas at 50 PSIG and 100 SCFH, hydrogen as the secondary plasma gas at 50 PSIG and 15 SCFH, nitrogen as the powder carrier gas at 50 PSIG and 15 SCFH. The current was 500 amps, at 77 volts and the spraying at a rate of 4-5 pounds per hour with a 3-4" spray distance.

The coating formed by spraying the first batch contained 72% zirconium oxide by volume, while the coating formed by spraying the second batch only contained 46% zirconium oxide by volum The coating formed by the first batch was of a substantially finer texture than that of the second batch.

Deponent having over 25 years experience in the flame spray field can state that powders in the millimicron size range cannot be considered flame spray powders and he

knows of no equipment which can satisfactorily spray such powders.

Further deponent sayeth not.

Ferdinand J Dittrich

Ferdinand J Dittrich

Subscribed and sworn to before me

this ___ day of _____, 1964

_____

E 341

Part 3 Pap #13

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 134 544 Group 110

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

AFFIDAVIT

STATE OF NEW YORK)
) SS:
COUNTY OF NASSAU)

ARTHUR P. SHEPARD, being duly sworn, deposes and says:

Deponent is a citizen of the United States, residing at Flushing, New York, and has been engaged as an engineer in the flame spraying field for over 30 years, and in view of this long and extensive experience states without qualifications or reservations that powders having a particle size in the millimicron range, as for example mentioned in U.S. patent 2 949 358, are not and cannot be considered flame spray powders and cannot be satisfactorily flame sprayed with any flame spray equipment known to him.

Further deponent sayeth not.

Arthur P. Shepard

Arthur P. Shepard

Subscribed and sworn to before
me this ____ day of _____, 1964

E 342

Metco 305.1
AS:as

NOV - 4 1964

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al.

Serial No. : 134,544

Filed : August 16, 1961 Group 110

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

October 30, 1964

Hon. Commissioner of Patents
Washington, D.C. 20231

Sir:

Supplemental to our amendment dated October 14, 1964, we enclose herewith for the record a further affidavit of Frank Nicholas Longo. This affidavit could not have been presented at an earlier date as the material used, i.e. the cobalt-clad tungsten carbide spray powder, was not available at the time the previous affidavit was executed and it was only prepared subsequent thereto for the purpose of the submitted affidavit.

Reconsideration and allowance of the application is hereby solicited.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

BY _____
Attorneys for Applicants

NOV 2 1964 PATENT OFFICE

AS:as

E 343 Part of #1

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al.

Serial No. : 134,544

Filed : August 16, 1961 Group 110

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

AFFIDAVIT

STATE OF NEW YORK)
) ss:
COUNTY OF NASSAU)

FRANK NICHOLAS LONGO being duly sworn, deposes and says:

Deponent on October 13, 1964 executed an affidavit in the above entitled application. In said affidavit deponent pointed out that in Experiment 1 nickel-coated tungsten carbide was used, as this was the only available coated tungsten carbide at the time the experiments were run. After completing the experiments, however, deponent proceeded to prepare a batch of powder consisting of tungsten carbide particles coated with cobalt. This batch of powder was identical to the second batch of powder described in deponent's affidavit of October 13, 1964 except that cobalt was used in the coating in place of the nickel. Deponent then proceeded to spray this batch of cobalt-clad tungsten carbide powder in the identical manner, with the identical equipment, and under the identical conditions as described in Experiment

E 344

I of deponent's previous affidavit. The deposit efficiency obtained was 58%.

Further deponent sayeth not.

Subscribed and sworn to
before me this [illegible] day
of [illegible] 1964.

Frank Nicholas Jargo

Notary Public

[illegible] York

[illegible] 1966

L 345

382 64

IN THE UNITED STATES PATENT OFFICE

Applicant : FERDINAND J. DITTRICH, et al

Serial No. : 134,344

Filed : August 16, 1961 ~~Div.~~ Group 110

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

Date: November 20, 1964

Hon. Commissioner of Patents
Washington 25, D. C.

REJECTED CLAIMS: 24, 28, 31-35, 40, 44 and 68-72

Sir:

Applicant(s) hereby appeal to the Board of Appeals from the decision of the Examiner finally rejecting the above claims.

Check for $25.00 to cover appeal fee is enclosed.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

BY _____
Attorneys for Applicants

E 346

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

Appeal No. : 38 264

Filed : November 23, 1964

In re application of : Ferdinand J. Dittrich et al

Serial No. : 134 544

Filed : August 10, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

Group : 110

December 28, 1964

BRIEF ON APPEAL

This is an appeal from the Action of the Primary Examiner, dated July 24, 1964, finally rejecting the claims in the above application.

An oral hearing is respectfully requested.

THE CLAIMS

The finally rejected claims involved in this appeal are as follows:

24. A flame spray powder in the form of individual, synergistically clad particles of a size between about 60 mesh and plus 5 microns comprising a nucleus and at least one coating layer of a material differing from said nucleus, one of said coating layer and nucleus comprising a refractory selected from the group consisting of refractory oxides, refractory carbides, and diamond, the other a bonding matrix for said re-

fractory material selected from the group consisting of nickel and cobalt matrices.

28. A flame spray powder according to claim 24 in which said nucleus comprises a refractory material and said coating comprises a bonding matrix for the material of said nucleus.

31. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus is a refractory material.

32. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus is a carbide.

33. A flame spray powder according to claim 32 in which said carbide is tungsten carbide.

34. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus is aluminum oxide.

35. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus is diamond.

40. A flame spray powder according to claim 24 in which said powder is bonded in the form of a wire.

44. A flame spray powder according to claim 24 including at least one additional coating layer differing from said nucleus and first mentioned coating layer and synergistically active with at least one of said nucleus and first mentioned coating layer in flame spraying.

68. Flame spray powder according to claim 24 in which said refractory material is a refractory oxide.

69. Flame spray powder according to claim 68 in which said refractory oxide is a member selected from the group consisting of alumina and zirconia.

70. Flame spray powder according to claim 24 in which said refractory material is a refractory carbide.

71. Flame spray powder according to claim 70 in which said refractory carbide is tungsten carbide.

72. Flame spray powder according to claim 24 in which said refractory material is diamond.

THE CITED ART

The art cited by the Examiner in support of the Final Rejection is as follows:

Alexander et al	2 949 358 Aug. 16, 1960 (Filed Sept. 23, 1957)	75-176
Sheildon	3 006 782 Oct. 31, 1961 (Filed March 9, 1956)	29-195
Dawson	3 023 490 March 6, 1962 (Filed Nov. 25, 1955)	29-195
Poorman et al	2 714 563 Aug. 2, 1955	29-194

THE INVENTION

The applicants' invention as covered by the rejected claims is directed to an improved flame spray powder for producing a refractory containing coating by the flame spray process.

Flame spraying is a well known and commercially practiced process for producing coatings on surfaces. The process basically involves the feeding of a heat-fusible material, such as a metal, into the heating zone of a flame spray gun where the same is melted or heat-softened, and then sprayed from the gun against the surface to be coated. The heat-fusible material may initially be in the form of a wire or rod, in which case a wire-type flame spray gun is utilized, or may be in the form of powder in which case a powder-type gun is utilized.

In the early years of its development the flame spray process was predominantly used for spraying metals and is thus some times referred to as "metal spraying" or "metallizing". In more recent years the spraying of refractories, such as refractory oxides and carbides has become commercially wide spread.

In flame spraying in order to produce a satisfactory coating, the material being sprayed must be sufficiently heated to allow the sprayed particles to stick to the surface forming an adherent coating. Furthermore, to be economically feasible an excessive quantity of the sprayed particles should not bounce off the surface. The percentage of the particles sprayed which stick to the surface forming the coating is referred to in the art as the "deposit efficiency" and, of course, a satisfactory flame spray material must be capable of being sprayed with a relatively high deposit efficiency.

When attempting to spray high melting materials, such as refractories, utilizing for example flame spray guns operated

with the conventional combustion flame, such as oxyacetylene flames, it was often not possible to achieve sufficiently high temperatures to spray the high melting refractory materials and in many instances these refractory materials would not adhere to the base, or would only adhere with low deposit efficiency.

In order to produce adherent flame spray coatings containing refractories such as refractory oxides or carbides, it was customary to utilize rather than a pure refractory, a refractory admixed with a lower melting point metal which would act as a bonding matrix. For this purpose nickel and cobalt were most commonly used as the bonding matrix. The nickel or cobalt would become sufficiently heat-softened or melted so as to form the sprayed coating and the refractory particles would be embedded and bonded in this matrix even if the same were not sufficiently melted or softened per se. Most commonly the matrix containing refractory flame spray powders were in the form of aggregates, i.e. powder particles consisting of individual sub-particles of the refractory bonded together with the nickel or cobalt matrix.

The applicants' invention is directed to a novel form of the matrix-refractory particles, this form consisting in contrast to the conventional aggregates, of individually clad particles, each of the particles consisting of a nucleus and a coating layer. Thus the nucleus may consist of the refractory which in accordance with the claimed invention is limited to a refractory oxide, carbide, or diamond, and the

layer of the matrix which in accordance with the claimed invention is limited to nickel or cobalt. In this particular form as compared with the conventional aggregates, or simple mixtures of the refractories and the matrix, the powder may be flame sprayed to form a dense adherent coating with a greater deposit efficiency than could previously be achieved.

In addition to the discovery that the refractory oxides or carbide can be sprayed in this form, the applicants have discovered that diamond can also be sprayed in this form. The diamond, of course, cannot be heat-softened and thus is incapable of being flame-sprayed. When incorporated however, in the particular form of the clad particles in accordance with the invention, the same may be sprayed to form high grade coatings with a high deposit efficiency.

The powder in accordance with the invention is, of course, used in conventional flame spray applications for refractory materials, i.e. where wear and heat resistant coatings are desired, or as coatings used for grinding, cutting and abrasive purposes.

THE CITED ART

The Alexander et al patent 2 949 353 relates to a metal composition consisting of molybdenum, rhenium or tungsten having submicron refractory particles dispersed therein, the metal composition being intended for the fabrication of oxidation resistant metal products as, for example, by powder metallurgy techniques.

The Dawson patent No. 3 025 490 relates to an armored coating base having hard refractory carbide particles embedded in a matrix alloy, such as Stellite. In accordance with Dawson the armored coating is produced by initially coating the article with a shellac solution containing a mixture of the refractory carbide particles, the matrix and a flux, and then fusing this coating in place.

The Sheildon patent 3 000 782 relates to the initial flame spraying of a metal undercoat, such as nickel nichrome, or the like, which is followed by the over-spraying of refractory metal oxide particles, the oversprayed particles in this over-spraying operation being heated to molten temperature.

The Poorman et al patent 2 714 563 relates to a special coating technique which may be termed a detonation in which the coating material is actually fired at high velocity against a surface to be coated. Refractory materials such as tungsten carbide (in the form of an aggregate containing cobalt) are among the materials mentioned in the patent which may be used for forming by the detonation technique.

THE GROUNDS OF THE REJECTION

In rejecting the claims the Examiner has taken the position that the Dawson and Alexander et al patents which were cited as primary references disclose clad powders in which a nucleus comprises a refractory material and the

coating a bonding matrix for the material of the nucleus and that the Sheiffer and Poorman et al references disclose that it is old to use refractory powders in flame spraying so that it would not involve invention to use the powders of Dawson and Alexander et al for flame spraying.

ARGUMENTS

Initially it is pointed out that the Dawson patent, contrary to the Examiner's statement, does not disclose a clad powder in which the nucleus comprises a refractory material and the coating a bonding matrix for the material of the nucleus. In Dawson the powder disclosed is simply a powder mixture of the refractory, a matrix and a flux which is additionally mixed with the thinned shellac for applying a paint-type coating. There is absolutely no disclosure of individual powder particles comprising a nucleus of a refractory and a coating layer of a bonding matrix for the refractory. While Dawson ultimately produces a coating termed an armored coating consisting of the matrix with dispersed refractory particles, this is formed by fusing the shellacked coating and not be a flame spray technique.

Dawson, thus, at best can be cited as showing a simple mixture of refractory and matrix particles and reference is made to the Longo affidavit of record executed October 13, 1964, where it is shown that a mixture of tungsten carbide and matrix particles cannot be satisfactorily flame sprayed to form a coating containing a significant amount of the refractory whereas, the same components in the form of the clad particles

in accordance with the invention may be sprayed with a high deposit efficiency produce a coating containing a high content of the refractory particles.

The Alexander et al patent has nothing to do with flame spraying, but in contrast thereto, relates to a metal composition which may be worked by powder metallurgy techniques to initially form billets, sheets or rods, which are further, hot or cold, worked by known metallurgical techniques to form articles. In the production of this metal composition the patentee may pass through a stage in which there is formed a powder consisting of refractory oxide particles coated with a metal. In the first place, however, the coating metal is either molybdenum, rhenium, or tungsten and is thus not the cobalt or nickel matrix called for in the applicants' claim, and in the second place the particles are of a sub-micron size and, as is shown by the Dittrich, Longo, Shepard, and Ingham Jr. affidavits of record, all executed October 13, 1964, these sub-micron particles may not be considered flame spray particles and may not be satisfactorily sprayed.

The secondary references to Wheildon and Poorman et al have only been cited to show the flame spraying of refractory powders and admittedly do not show coated powders in accordance with the invention. It is the Examiner's position that in view of the secondary references showing the use of refractory powders in flame spraying it would not involve invention to utilize the powders of Dawson or Alexander et al for flame spraying. Dawson, however, as mentioned, simply shows a powder mixture, and Alexander et al does not disclose a composite

having the components called for in the applicants' claims and does not disclose a powder suitable for flame spraying as the same is substantially smaller than the particle size called for in the applicants' claims, i.e. is a submicron particle in the millimicron range and, as shown by the affidavits, is not suitable for flame spraying.

The affidavits of record, including the supplemental Longo affidavit executed October 28, 1964, show that the clad powders claimed by the applicants produce substantially improved results in flame spraying, allowing spraying with a much higher deposit efficiency as compared with the conventional aggregates or mixtures. Thus, in the face of this record it is not deemed how the applicants' novel clad powders could be considered obvious from the cited art.

CONCLUSION

The applicants' specifically claimed clad flame spray powders are not taught in the prior art and would not be obvious therefrom and are thus patentable, so that the Examiner should be reversed and the claims allowed.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

PAPER NO. ..6

U.S. PARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications regarding this application should give the serial number, date of filing, name of the applicant, and appeal number.

E 356

In re application of
[illegible] J. Dittman
et al.
Ser. No. [illegible]
Filed [illegible]
For [illegible] SPRAYING SYNERGISTIC COMPOSITES

Appeal No. [illegible]

Before the Board of Appeals

[illegible], Hindley and Sprung
for appellants

MAILED
MAY - 6 1965
[illegible]

Examiner's Answer

This is an appeal from the final rejection of claims 2-, 2-, 1-[illegible], -0, -, -, -2 all of the claims which are [illegible].

Claimed

A correct copy of the appealed claims appear on page 1-[illegible] of appellants' brief.

References

The references of record relied on are:

[illegible] Poorman et al.
[illegible] Underwood
[illegible] Hindin et al.
[illegible] Morton.

117/105.2 Rad

The [illegible]

The [illegible] recited in the appealed claims are on page 1-[illegible] of the appellants' brief.

U.S. GOVERNMENT PRINTING OFFICE: 1963—O-710-419
GPO 875-831

Description of References Poorman et al. teaches the use of various metal powders in flame spraying such as cobalt and tungsten carbide and the size of the powder for flame spraying. Column 5, lines 62-75.

Bradstreet teaches that it is old to flame spray powders of very small size as low as 2 microns. Column 5, lines 3[illegible] to 73.

Alexander et al. discloses a powder consisting of refractory oxide particles coated with a metal differing from said particles. Column 2, lines 39-41, column 5, lines 40-71, and column 6, lines 25-[illegible].

Sheldon discloses that it is old and well known to flame spray refractory metal oxides and metal of the group nickel and cobalt for [illegible] heat resistant oxidation resistant alloy coating. [illegible], lines 19-34 and column 7, lines 25-[illegible].

The Rejection

Claims 2[illegible], 24, [illegible], 30, 34, 61-72 are rejected under 35 U.S.C. 103 as unpatentable over Alexander et al. in view of Sheldon, Poorman et al. and Bradstreet. The basic reference discloses powder composed of individually clad particles, each of the particles consisting of a nucleus of a refractory oxide and a coating of a refractory metal. Column 2, lines 39-41. Poorman et al. teaches the use of various metal powders in flame spraying such as cobalt and tungsten carbide and the size of the powders for flame

spraying. Wheildon further teaches that it is old and well known to flame spray refractory metal oxides and metal from the group nickel and cobalt to form a heat resistant oxidation resistant alloy coating. Bradstreet is cited only to show that it is old and well known to flame spray powders of very small size as low as 2 microns. Therefore in view of the teachings of the secondary references it would not be invention to use the clad powders of the form of the basic reference in flame spraying because that is what the prior art teaches can be done. But more importantly the examiner points out that no patentable import at all can be given to the recitation in the claims of the intended use of the clad powders because it is but an indication of the broad field of contemplated use and is not a limitation to be considered in the question of patentability. The discovery or invention of a new use of a known composition of matter or material may be patentable, but such use can be nothing other than a method or process. As a matter of claim drafting the discoverer of a new use must protect his discovery by means of process or method claims and not product claims. In re Hack, 721 O.G. 422, 114 U.S.P.Q. 161, [illegible] C.D. 334. Therefore it is felt that the basic reference is an anticipation of the claimed subject matter because it teaches the same form (clad) of the powder as the appellants claim.

Discussion

The appellants' basic contention is that the Alexander et al. reference does not disclose that his clad powders can be used for flame spraying. Last paragraph page 5 and first two complete paragraphs of page 6 of the brief. The examiner agrees with this argument by the appellants but contends that a grant of a patent on composition cannot be predicated on a new use of a composition. Although adaptation to a new use may involve invention, patent on old product, based on its new use, has never been authorized by patent laws which provided for patents only on new and useful composition of matter, or any new and useful improvement thereof. The 1952 Act does not limit or modify this doctrine. While it recognizes that discovery or invention of a new use of a known composition of matter, or material may be patentable such use can be nothing other than a method or process. Therefore, the discoverer of a new use must protect his discovery by means of process or method claims not product claims. In re Hack, 721 O.G. 422, 114 U.S.P.Q. 161, 1957 C.D. 554.

All the other arguments of the appellants are in support of this basic argument about the use of the clad powders for flame spraying. Thus it is stated that the clad powders of the Alexander et al. patent are to small to be flame sprayed and the appellants point to affidavits to prove this. The affidavit of

E 360

Ingham is an opinion affidavit only and asserts that powder above at least 3 microns is needed for flame spraying. The Bradstreet patent was cited to show that powder as small as 2 microns has been satisfactorily sprayed. The affidavits of Longo are insufficient because they / compare a coated powder with a mixture of powders or a matrix-bonded powder and the Alexander et al. powder is a coated or clad powder. Column 2, lines 39-41. The affidavit of Dittrich is insufficient for the same reasons as the Longo affidavit. The affidavit of Shepard is an opinion affidavit only. The examiner points out that the clad powders of the Alexander et al. reference are larger than 0.5 micron because that figure points only to the refractory oxide nucleus. Column 1, lines 22-24. Furthermore, the examiner notes that limitation as to size is not patentably significant. In re Lose, 65 O. G. [illegible].

The appellants further argue that the Alexander et al reference does not disclose their particular coating metal of cobalt or nickel although the patent does teach the form of the powder. The appellants on page 5, last paragraph say that their invention is a novel form of powder consisting of individually clad particles, each of the particles

consisting of a nucleus of a refractory compound and a coating layer. The same concept of the invention is found on page 5, second paragraph of the specification. There is nothing critical about the nickel or cobalt coating as is disclosed on page 6, of the specification. The examiner points out that the nickel and cobalt is further a function of the use in flame spraying because as the appellants disclose on page 6 of the brief in conventional flame spray applications for refractory materials where wear and heat resistance is desired nickel and cobalt are commonly used as taught by Wheildon in column 7, lines 29-65. Poorman et al. further teaches that molybdenum and tungsten are commonly used refractory materials in flame spraying. Column 5, lines 42-75. Thus the difference between the coatings of the appellants powder and the Alexander et al. reference is in degree only. The Alexander et al. reference clearly discloses the alleged novel form of the matrix-refractory particles of the appellants, namely, individually clad particles, having a refractory oxide nucleus and a metal coating. Last paragraph, page 5 of the brief.

In conclusion it is pointed out that the appellants are here attempting to procure a patent based on their discovery that a known composition of

Serial No. 134,544
Appeal No. 382-64

matter can be adapted to use in flame spraying. Their claims are product claims. To entitle him to a patent the composition claimed must be both new and unobvious to one skilled in the art. In the view of the Examiner it is neither.

It is submitted that these claims were properly finally rejected. Accordingly, an affirmance of the rejection is respectfully solicited.

Respectfully submitted,

David L. Reck
Examiner

KOW

RODean:mjs

Conferee: M. Markva

WO 1-3621

E 363

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

Appeal No. : 38 264

Filed : November 23, 1964

In re application of : Ferdinand J. Dittrich et al

Serial No. : 134 544

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

Group : 110

May 18, 1965

REPLY BRIEF

In the Examiner's Answer the Examiner lists the Bradstreet patent 2 904 449 as a reference of record. Bradstreet is not of record and is newly cited. This reference has been cited by the Examiner to show that it is old to flame spray powders of a very small size. A study of the portion of Bradstreet relied on by the Examiner, i.e. Col. 5, lines 36 to 73, will show that Bradstreet indicates that the lowest limit of sprayable size is between 2 or 3 microns, which is directly in line with and confirms the affidavits of record in this respect.

The applicants' position in connection with the Alexander et al reference, i.e. the primary reference, is not that Alexander et al does not disclose that his clad powders can be used for flame spraying, but that:

a) the powders cannot be used for flame spraying and thus are not the equivalent of the applicants' flame powders, and

b) that the point where Alexander et al produces clad powders is merely a transitory stage in his production.

Aside from the fact that Alexander et al does not teach flame spray powders as is admitted by the Examiner, the clad powders which he would produce at a stage in his process could not be used for flame spraying and are not equivalent of the claimed flame spray powders. These powders are of a sub-micron size and as shown by the affidavits of record and supported by the newly cited Bradstreet patent, such small powders are not suitable for spraying. The Examiner objects that the affidavits are "opinion affidavits". These affidavits are affidavits of established experts in the art and are based on their knowledge and experience. It can well be appreciated by the Board that these affidavits are the only types of affidavits which would be suitable to show that the sub-micron particles cannot be satisfactorily flame sprayed. Innumerable experiments could be conducted showing unsatisfactory spraying of such particles, but such affidavits would merely prove that the particles were not sprayable in the particular equipment tried, and would not necessarily be applicable to other equipment. The best way of proving that these smaller particles are not flame spray particles is by affidavits of

experts of the type filed herein.

With respect to the Longo affidavits, the same have been offered to show that the clad particles as claimed in accordance with the invention produced new and unexpected results as compared with the same components in different form.

In their main brief the applicants have pointed out that the Alexander et al reference does not disclose the coating metal of cobalt or nickel and this is admitted by the Examiner.

In connection with the Examiner's contention to this argument and the combination applied by the Examiner to show the substitution of nickel and cobalt, it is simply pointed out that the combination as made by the Examiner is per se improper as the artisan would never consider applying a teaching relating to the flame spray art to Alexander et al which relates to an entirely different art.

It is respectfully requested that the case be reversed and the claims allowed.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

U.S. DEPARTMENT OF COMMERC
PATENT OFFICE
WASHINGTON

Paper No. 18

E 366

June 14, 1965

Burgess, Dinklage and
Sprung
605 Third Avenue
New York City
New York, 10016

Appeal No.: 382-64
Appellant : Ferdinand Dittrich
Serial No. : 134,544 et al.

Hearing
Date: July 29, 1965
Time: 9:30
Place: 1801 K St., N. W.
Room 502

NOTICE OF HEARING
CONFIRMATION REQUIRED WITHIN TWENTY DAYS

The appeal in the above identified case will be heard by the Board of Appeals on the date indicated.

The hearings will commence at the time set and as soon as the argument in one case is concluded, the succeeding case will be taken up.

The time allowed for argument is thirty minutes unless additional time is requested and permitted before the argument is commenced.

By Order of the Board of Appeals.

James E. Crocker
Administrative Officer

NOTE: In order to make the most effective use of the Board's hearing facilities, CONFIRMATION OF THE REQUEST FOR ORAL HEARING, WHICH HAS BEEN SET AS NOTED ABOVE, IS REQUIRED WITHIN TWENTY DAYS FROM DATE OF THIS NOTICE.

Failure to do so will be construed as a waiver of the request for the hearing.

PLEASE REFER TO APPEAL NUMBER IN ALL COMMUNICATIONS CONCERNING THIS CASE

POL-38 (4-65)

121

USCOMM-DC 8368-P65

Metco 305.1
AS/sfg

E 367

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

BOARD OF APPEALS
JUL 7 1965
U.S. PATENT OFFICE

Appeal No. : 382-64

Filed : November 23, 1964

In Application : FERDINAND DITTRICH, et al

Serial No. : 134,544

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

Group : 110

June 30, 1965

In the above Appeal the applicants hereby waive the Hearing in the above matter and will rely solely on arguments presented in the Briefs.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

E 368

Group No. 110

Appeal No. 382-62

IN THE UNITED STATES PATENT OFFICE

BEFORE THE BOARD OF APPEALS

Ex parte Ferdinand J. Ulrich
and Arthur P. Bergerd

- - - - - - -

Application for patent filed August 16, 1961, Serial No. 134,564, which is a continuation in part of application Serial No. 72,543, filed November 22, 1960, now abandoned. Flame Spraying Synergistic Composites.

Burgess, Dinklage and Sprung for appellants.

Before Hall and Lilloff, Examiners-in-Chief and Vertiz, Acting Examiner-in-Chief.

Vertiz, Acting Examiner-in-Chief.

Appeal has been taken from the final rejection of claims 24, 28, 31 to 35, 40, and 68 to 72, all the claims remaining in this application.

Claim 24, the only fragmentary claim on appeal, reads as follows:

24. A flame spray powder in the form of individual, synergistically clad particles of a size between about 60 mesh and plus 3 microns comprising a nucleus and at least one coating layer of a material differing from said nucleus, one of said coating layer and nucleus comprising a refractory selected from the group consisting of refractory oxides, refractory carbides, and diamond, the other a bonding matrix for said refractory material selected from the group consisting of nickel and cobalt matrices.

The references relied upon by the Examiner are:

Poorman et al.	2,714,563	Aug. 2, 1955
Bradstreet	2,904,689	Sep. 15, 1959
Alexander et al.	2,949,358	Aug. 16, 1960
Wheildon	3,006,782 (Filed	Oct. 31, 1961 Mar. 9, 1956)

The subject matter of this appeal relates to a composite powder for use in a flame spray process in applying a refractory coating to a substrate.

In our opinion, the references relied upon by the Examiner do not disclose nor suggest the powder of the appealed claims.

Alexander et al., which is the primary reference, relate to a composition consisting of molybdenum, rhenium, or tungsten having refractory oxide particles dispersed therein to enhance oxidation resistance. We find no disclosure therein of individual metal clad refractory particles. Nor do we find a logical basis in the substitution of nickel or cobalt for molybdenum, rhenium, or tungsten as the claimed metal because the substitution would alter completely the nature of patentees' powder. Furthermore, Alexander et al. have no disclosure of the carbide required by claims 20, 33, 70 and 71, or the diamond of claims 32 and 72, or the

additional coating layer of claim 44. Claim [illegible] requires the powder to be border in the form of [illegible]ine. No specific holding has been made by the examiner with respect to this claim. Accordingly, we will not sustain the stated rejection on the present record.

It appears to us that the Examiner should consider class 252, subclass 406, before taking further action in this application, especially with regard to claims involving alumina clad with nickel or cobalt. We also call attention to the pertinency of class 75, subclasses 204 and 205 as well as to class 29, subclasses 182.7 and 182.8. The possibility of anticipatory art in these subclasses with respect to cobalt clad powder having a carbide nucleus is indicated by Goetzel in his "Treatise on Powder Metallurgy", Vol. II, pages 94 and 95, published by Interscience Publishers, Inc., New York, 1950.

The decision of the Examiner is reversed.

REVERSED

H. Ingraham
Examiner-in-Chief

Examiner-in-Chief

Examiner-in-Chief
(Acting)

BOARD OF APPEALS

Parmelee, Bicknell & Cramer
60 East Third Avenue
New York, N.Y. 10016

E 371

Paper No. 21

ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON, D.C. 20231

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

In Reply Please Refer To:

Burgess, Dinklage & Sprung
60[illegible] Third Ave.
New York, N.Y. 10016

Applicant:	
[illegible] T. Dittrich et al.	
Ser. No. [illegible]	[illegible]
Filed [illegible]	NOV 15 1965
For [illegible]	

Communication received May 20, 1965
(Date)

In view of applicant's communication filed on the date indicated above, the Examiner has reconsidered this application and found it allowable.

Prosecution on the merits is hereby closed and the Notice of Allowance or other appropriate communication will be sent in due course.

Donald E. Kech

Examiner

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POL-255 (8-64)

USCOMM-DC 7182-P64

E 372

FORM PO-12a
(9-1-50)

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE

#45

TITLE REPORT

110

NO. Ser. 134,544 c-p

NAME Ferdinand J. Dittrich

Arthur P. Shepard

THE TITLE APPEARS FROM THE ASSIGNMENT RECORDS TO BE VESTED IN:

Metco, Inc.,

a corp. of New Jersey.

EXAMINED UP TO AND INCLUDING Oct. 11, 1965

THIS CERTIFICATE DATED Dec. 27, 1965

SGD. F. TULE

HEAD OF ASSIGNMENT BRANCH

NO FURTHER ASSIGNMENTS APPEAR TO HAVE BEEN RECEIVED FOR RECORD INCLUDING:

127

COMM-DC 67106

Paper No.

...S ONLY
...NER OF PATENTS
...TON, D.C. 20231

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 373 C 3554 22/2

In Reply Please Refer To:

Burgess, Dinklage and
Sprung
605 Third Avenue
New York City, New York

Applicant: Ferdinand J. Dittrich et. al.

Ser. No. 134,544

Filed Aug. 16, 1961

For FLAME SPRAY CLAD POWDER COMPOSED OF A REFRACTORY MATERIAL AND NICKEL OR COBALT

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

The changes hereinafter specified have been made in the application identified above in accordance with the provisions of Order Number 3141 of February 4, 1930, (Manual of Patent Examining Procedure 1302.04), which reads in part as follows:

> Other obvious informalities in the application may be corrected by the examiner, but such corrections must be in the form of an amendment, approved and signed by the Principal Examiner, placed in the file, and made a part of the record. A copy of the amendment is sent to the applicant. The changes specified in the amendment will be entered by the clerk in the regular way.

If these changes are not satisfactory to the applicant, an appropriate amendment may be proposed under the provisions of Rule 312, provided the printing of the specification has not begun at the time such amendment is ready for entry. To insure the consideration of such amendment for inclusion, it should be submitted on or before the date of remitting the final fee since the printing of the specification begins a few days thereafter.

The application has been amended as follows:

Page 50, the last paragraph has been cancelled.

Page 1, before the first line of the specification, the following has been inserted: "This is a continuation-in-part of application Serial No. 72,543, filed November 22, 1960, now abandoned.

David L. Rick
Examiner

RODean:mb

WO7-3621

ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON, D. C. 20231

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 374

All communications regarding this application should give the serial number, date of filing, and name of the applicant.

NOTICE OF ALLOWANCE AND ISSUE FEE DUE

The application for patent identified below has been examined and found allowable for issuance of Letters Patent.

	FILING DATE	SERIAL NO.	NO. OF CLAIMS ALLOWED	EXAMINER (GROUP)
	08/16/61	134544	14	D. Reck 11
APPLICANT	Dittrich, Ferdinand J.; Bellmore, and Shepard, Arthur P.; Flushing, N. Y.			MAILED Jan. 20, 1966
TITLE OF INVENTION (X indicates as amended by examiner)	Flame spray clad powder composed of a refactory material and nickel or cobalt			
	DRAWING NO. SHEETS @ $2 EACH: 001	SPEC NO. PAGES @ $10 EACH: 13	ISSUE FEE DUE: $232	CLASS SUB: 029/183.5

With the allowance of the application, the above indicated Issue Fee becomes due and payment must be made within three months of the date of this Notice or the Patent will become abandoned (forfeited).

The Issue Fee is one hundred dollars ($100) plus two dollars ($2) for each printed sheet of drawing and ten dollars ($10) for each printed page of specification, or portion thereof.

Inasmuch as the number of printed pages of specification must be determined in advance of printing from the amount of matter in the allowed application, the Issue Fee is subject to change. After the patent has been printed, the estimate will be reviewed in light of the actual number of pages of specification. If it is found that an overcharge was made, you will be notified thereof with the issuance of the Patent and a refund will be forthcoming. If the number of pages is underestimated by two or more pages, you will receive a notice of Additional Issue Fee Due with the Patent and payment of this amount must be made within three months of the date of that Notice. Failure to remit any additional fee due within three months from the date of that Notice will result in lapse of the Patent.

As a convenience in remitting this fee, use of the enclosed Form POL-85a is suggested. The Issue Fee will not be received from anyone other than the applicant, his assignee or attorney, or a party in interest as shown by the records of the Patent Office. A form is enclosed relating to the address of the inventor(s) which requires your attention.

If it is desired to have the patent issued to an assignee or assignees, an assignment, together with the fee for recording the same, must be filed in this Office on or before the date of payment of the Issue Fee.

The patent will be issued and forwarded within approximately two months after receipt of the Issue Fee.

By direction of the Commissioner.

Burgess, Dinklage, et al
605 Third Ave.
New York City, New York 10016

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REFERENCES CITED BY EXAMINER

The following references, cited by the examiner, are of record in the patented file of this patent:

UNITED STATES PATENTS

PATENT NUMBER	DATE	NAME OF PATENTEE	OFFICIAL CLASSIFICATION
1,986,197	1-1935	Harshaw	75-0.55
2,288,869	7-1942	Wasserman	117-46
2,359,401	10-1944	Wulff	75-0.55
2,612,581	9-1952	Robinson	29-191
2,714,563	8-1955	Poorman et al.	29-194
2,904,449	9-1959	Bradstreet	117-105.2
2,908,589	10-1959	Gutzeit	117-46
2,933,415	4-1960	Homer et al.	29-191
2,936,229	5-1960	Shepard	75-0.55
2,949,358	8-1960	Alexander et al.	75-176
3,006,782	10-1961	Wheildon	29-195
3,023,490	3-1962	Dawson	29-195

FOREIGN PATENTS

PATENT NUMBER	DATE	COUNTRY

OTHER REFERENCES

(List the following items when available, page number, date, and title)

130

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

Paper No. : 24

E 376

Serial No. : 134,544

EXAMINER(S) NAMED IN ALLOWED APPLICATION

The examiners with full or partial signatory authority whose signatures appear upon the actions in this allowed application are named below. Their names shall appear, as given below, on the printed copies of the patent specification and claims as the final matter thereon.

DAVID L. RECK	Primary Examiner
WILLIAM D. MARTIN	Examiners
HYLAND BIZOT	
~~DAVID L. RECK~~	XXXXXXX
V. E. SULLIVAN	Assistant Examiners
R. O. DEAN	

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USCOMM-DC 7022-P64

U.S. Department of Commerce
Patent Office

E 377

ISSUE FEE TRANSMITTAL

Effective convenience in transmitting Issue Fees to the Patent Office. When properly completed it may be used in lieu of transmittal letter. Respondents will note and fill in items numbered 1 thru 5 below. The Issue Fee Receipt will be mailed to the address appearing in box at lower left of this form. If desired, use the reverse side of this form for carbon copy when completing this form.

COMMISSIONER OF PATENTS is requested to apply the accompanying fee to the case identified below, and deliver the patent as indicated.

BURGESS, DINKLAGE & SPRUNG

April 13, 1966
Date

By _____
Attorney or Applicant

NOTE--Issue Fees will not be received from other than the applicant, his assignee, or attorney, or a party in interest as shown by the records of the Patent Office. Issue Fees will not be applied to pending applications.

	FILING DATE	SERIAL NO.	NO. OF CLAIMS ALLOWED	EXAMINER
	08/16/61	134544	14	D. Rock 11
APPLICANT	Dittrich, Ferdinand J.; Bellmore, and Shepard, Arthur P.; Flushing, N. Y.			MAILED Jan. 20, 1966
TITLE OF INVENTION (X indicates as amended by examiner)	Flame spray clad powder composed of a refactory material and nickel or cobalt			NOTICE OF ALLOWANCE DATE
	DRAWING: NO. SHEETS @ $7 EACH: 001	SPEC: NO. PAGES @ $10 EACH: 13	ISSUE FEE DUE: $232	CLASS-SUB: 029/183.5

2. Assignee: (If assigned and name does not appear in the corresponding space above)

METCO, INC.

3. FEE ENCLOSED

$ 232.00

REFUND SCHEDULED
$ 46.00 JUN 7 1966
(By Treasury check is approximately ten (10) days from above date)
CERT. ACCOUNTING OFFICER
PATENT OFFICE

MAILING INSTRUCTIONS

NOTE--The office will send the patent to the address entered in stub at left below unless you direct otherwise. Use the space provided to indicate any changes which affect the delivery of the patent. However, if an additional Issue Fee Due Notice is required, this option is cancelled and the patent will be mailed to the address entered in the stub at left below.

4 Do not send the patent to the addressee listed below. Send patent to (check one)

☐ Patentee
☐ Assignee
☐ Associate Attorney (See specific authorization in file)
☐ Change of address Attorney

The address of the person checked above is typed in Item 5 below

132

5. (If an additional Issue Fee is required the patent will not be sent to this address)

APR 15 1966
U.S. PATENT OFFICE

BURGESS, DINKLAGE & SPRUNG
Attorneys
605 THIRD AVENUE
NEW YORK, N. Y. 10016

E 378

Date: April 13, 1966

Hon. Commissioner of Patents
Washington 25, D. C.

ON ALL PAPERS PLEASE
FURNISH OUR FILE NO.
METCO 305.1

Dear Sir:

Re the application of FERDINAND J. DITTRICH and ARTHUR P. SHEPARD

for FLAME SPRAY CLAD POWDER COMPOSED OF A REFRACTORY MATERIAL AND NICKEL OR COBALT

we enclose

( ) Specification — Serial No. : 134,544

( ) Declaration, Power of Attorney and Petition — Filed : 8/16/61

( ) _____ Sheet(s) Drawings — Group : 110

( ) _____ Claim(s) in excess of 20

( ) $ .00 filing fee (covered by enclosed check)

( ) Assignment

( ) $3.00 recording fee (covered by enclosed check)

( ) Authorization to furnish references cited in office actions
(X) Supplemental Declaration
( ) Priority is hereby claimed on the basis of the following:

Country	Serial No.	Date

Respectfully,

BURGESS, DINKLAGE & SPRUNG

BY Charles Sprung Reg

134

JOINT SUPP.

E 379

IN THE UNITED STATES PATENT OFFICE

Applicants: FERDINAND J. DITTRICH, et al

Serial No.: 134,544

Filed: August 16, 1961 Gr. 110

For: FLAME SPRAY CLAD POWDER COMPOSED OF A REFRACTORY MATERIAL AND NICKEL OR COBALT

SUPPLEMENTAL DECLARATION

We, the undersigned, declare with respect to the above-entitled application that the subject matter of the allowed claims was part of our invention, was invented before we filed our original application, above-identified, for such invention; that we do not know and do not believe that the same was ever known or used before our invention thereof, or patented or described in any printed publication in any country before our invention thereof, or more than one year before our application, or in public use or on sale in the United States more than one year before the date of our application, that said invention has not been patented in any foreign country before the date of our application on an application filed by us or our legal representatives or assigns more than 12 months prior to our application in the United States, and has not been abandoned.

The undersigned petitioners declare further that all statements made herein of their own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 3 February 1966 Inventor: F. J. Dittrich (Signature)
Ferdinand J. Dittrich (sign exactly as typed)

Date: 3 February 1966 Inventor: Arthur P. Shepard (Signature)
Arthur P. Shepard (sign exactly as typed)

Date: _____ Inventor: _____ (Signature)
(sign exactly as typed)

Date: _____ Inventor: _____ (Signature)
(sign exactly as typed)

PATENT OFFICE
WASHINGTON, D.C. 20231

E 380

PATENT ISSUE FEE REFUND NOTICE

(Communications regarding this notice should refer to Patent No. and Date of this notice)

Patent Number
3254970
Date of this notice
June 7, 1966

Review of the printed pages of the above identified patent indicates the following issue fee overpayment:

ISSUE FEE	OVERPAYMENT
[x] Printed pages of specification	$. 40.00
[ ] Printed pages of drawing	$
[ ] Basic issue fee	$
Total if more than one fee	$

[x] A check in the amount of the overpayment will be mailed in the near future.

[ ] A credit in the amount of the overpayment will be made to your deposit account.

By Direction of the Commissioner of Patents

PLEASE FURNISH YOUR ZIP CODE IN ALL CORRESPONDENCE - IT IS AN ESSENTIAL PART OF YOUR ADDRESS

FORM POL-307 (3-68) USCOMM-DC 47279-P66

135

JUL 8 1966

E 381

Applicants : [illegible]

Serial No. : 134,[illegible]

Filed : August 16, 1[illegible]

For : [illegible]

Patent No. 3,254,[illegible] Issued: June 7, 1966

July [illegible], 1[illegible]

Com. Commissioner of Pat[illegible]
Washington, D.C. 20231

Sir:

The following [illegible] appears [illegible] in the printed [illegible] Patent No. 3,254,[illegible] issued June 7, 1966:

Column [illegible], line [illegible] should be --cu.--

(page 32, line 49)
Column 12, line 2[illegible] should be --nitrate--

(page 38, line 2)
Column 14, line 33, [illegible]anthanum should be --lanthanum--

(page 41, line 6)
Column 16, line 13, [illegible]anthan should be --lanthanum--

(page 41, line 42)
Column 17, line 47, chromium should be --chromium--

(page 4[illegible], line 2 from bottom)

[illegible] not [illegible] would warrant a [illegible] respectfully request [illegible] that [illegible] be entered in the file wrapper.

Respectfully submitted,
[illegible], BRINKMAN & [illegible]

[illegible]
Attorneys for Applicants
Address

13

E 382

IN THE UNITED STATES PATENT OFFICE

PATENT OFFICE
FEB 2 1972

U. S. Patent No. : 3,254,970

Issued : June 7, 1966

Patentees : F. J. DITTRICH et al

N O T I C E

The patentee of the above-identified patent would like to make of record the following patents and publications which are known and which relate to the field of the invention of the patent and/or which were cited during foreign patent office proceedings concerning related foreign applications.

This art was not made of record during prosecution of the application which matured into patent, as at that time it was not the practice to cite such non-anticipatory art.

It is respectfully requested that this Notice with the cited art be entered into the file wrapper of the patent for use by the public.

Country	Patent No.
Australia	210,300
Australia	208,224
Australia	213,359
Australia	228,798
Great Britain	746,384
Great Britain	666,315
Great Britain	575,449
Great Britain	574,124
Great Britain	419,960
Austria	204,794
Germany	DAS 1,020,506
Germany	384,717
Great Britain	551,689
Great Britain	842,280
Great Britain	543,773
Austria	172,317
Austria	179,938
Great Britain	410,300
Great Britain	591,880
France	1,203,277
Great Britain	604,457
Holland	13,905
France	977,747
Belgium	555,939
France	1,006,285

Country	Patent No.
France	1,194,596
Japan	Patent Publication 6525/60
Japan	Patent Publication 10563/57
Germany	DAS 1,029,212
France	1,169,865
Great Britain	798,605
Great Britain	1,000,353
Great Britain	784,967
Great Britain	783,435
Great Britain	776,853
Great Britain	433,095
France	1,313,303
United States	1,379,063
United States	2,853,403
United States	2,884,688
United States	2,910,356
United States	2,933,415
United States	3,025,182
United States	3,050,409
United States	3,121,643
United States	3,135,626
United States	2,231,247
United States	2,904,449
United States	2,936,229
United States	2,976,166
United States	2,988,807

Country	Patent No.
United States	3,049,435
United States	3,102,044
United States	1,986,197
United States	2,288,869
United States	2,359,401
United States	2,612,581
United States	2,714,563
United States	2,908,589
United States	2,949,358
United States	3,006,782
United States	3,023,490

Publications

Standard State of Binary Alloys

by Iwase Okamoto.

Constitution of Binary Alloys

by Hansen 1958.

Thermochemical Data of Alloys

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Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

February 1, 1972

by _____
Attorneys for Patentees

In Re [illegible]

United States District Court

for the
EASTERN DISTRICT OF N.Y.

E 387

COMMISSIONER OF PATENTS,
Washington 25, D. C.

SIR:

In compliance with the Act of July 19, 1952 (66 Stat. 814; 35 USC 290), you are advised that there was filed on the 25th day of APRIL, 19 73, in this court an action, No. 73C561, entitled:

Name EUTECTIC CORPORATION & ANO., Plaintiff,

Address 40-40 172nd ST., FLUSHING, N.Y., 11358

versus

Name METCO, INC., Defendant,

Address 1101 PROSPECT AVE., WESTBURY, LONG ISLAND, NEW YORK

brought upon the following patents:

TRADEMARK	DATE OF TRADEMARK	TRADEMARK-ee
1. ROTOTEC	not known	EUTECTIC CORP.
2. EXOTEC	not known	EUTECTIC CORP.
3.		
4.		
5.		

In the above-entitled case, on the day of , 19 , the following patents have been included by (insert amendment, answer, cross bill, or other pleading):

PATENT NO.	DATE OF PATENT	PATENTEE
1.		
2.		
3.		
4.		
5.		

In the above-entitled case the following decision has been rendered or judgment issued:

LEWIS ORGEL
Clerk.

Date APRIL 25, 19 73

By [signature]
Deputy Clerk.

SEARCH

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REFERENCE SEARCHED

C...	SUB.	DATE	EX'R
15	C.5 170 .76 [illegible] 212	11/12/65	ROL
29	193.5 191, 191.2 [illegible] 195		
117	200 130 131 116 165.2 [illegible]		

Parent Unassigned
10-11-65

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1.	Application ____ papers.	26.	Supp. Decl. Apr. 15, 1966
2.	Exmt Sept. 14, 1961	27.	Letter re: re-exam July 8, 1966
3.	Rec Restr R Sept 11, 1962	28.	Letter re Errors 2-3-72
4.	Restriction SEP 19 1962	29.	Notice of Suit April 25, 1973
5.	Rec'd R Nov 26, 1962	30.	
6.	ACTION JAN 3 1963	31.	
7.	Rec'd. 6 7/2/64	32.	
8.	Change of Address 7/6/64	33.	
9.	FINAL REJECTION JUL 24 1964	34.	
10.	Exmt 37 (6th) Dec. 31, 1964	35.	
11.	ANSWER SEP 14 1964	36.	
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14.	1.382 64 Nov 23, 1964	39.	
15.	Exmt (7) Jan. 7, 1965	40.	
16.	EXAMINER'S ANSWER MAY - 6 1965	41.	
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18.	Decision July 29 1965 A	43.	
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20.	DECISION BY BOARD OCT 29 1965 Revised	45.	
21.	LETTER POL 3:5 NOV 15 1965	46.	11/12
22.	EXAMINER'S AMENDMENT C JAN 12 1966	47.	
23.	LIST OF REFERENCES	48.	
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16—11570-7 U. S. GOVERNMENT PRINTING OFFICE

$40.00 REFUND SCHEDULED
JUN 7 1968
By Treasury check in appropriate amount

ABANDONED
E 390

237786 SERIAL NO.	P. R. Div.		PATENT NUMBER
Assistant examiner	Class 117	Subclass 104	DATED
Division No. 25	Filed (Date) OCT. 26, 1962	237786	CLAIMS FOREIGN PRIORITY: Country / Date

Applicant(s)

DITTRICH, FERDINAND J. OF BELLMORE, N. Y.

SHEPARD, ARTHUR P. OF FLUSHING, N. Y.

Number claims allowed	Print claim(s)	Class	Subclass

Assignor to

Title of invention

FLAME SPRAYING SYNERGISTIC COMPOSITES

☐ Division of ☐ Continuation of ☐ Continuation-in-part of

☐ Substitute for abandoned

Rule 147

APPLICATION Serial No.	Filed	APPLICATION Serial No.
/		

Sh. drw.	Extra claims	Filing fee	Transaction	Atty's docket
1	19	$49	47894	METCO 505.2

Now Patent No.	Granted	Filed

Send correspondence to:

BURGESS, DINKLAGE & SPRUNG

233 BROADWAY

NEW YORK 7, N. Y. 10016

Principal attorney(s)

BURGESS, DINKLAGE & SPRUNG

Associate attorney(s)

PARTS OF APPLICATION FILED SEPARATELY

PART FILING FEE $48	OCT. 16, 1962
PAPERS	OCT. 16, 1962
1 SHEET DRAWING	OCT. 16, 1962
PROPOSED AMENDMENT	OCT. 16, 1962
BAL. FILING FEE $1	OCT. 26, 1962

PREPARED FOR ISSUE

(Assistant Examiner) (Docket Clerk)

EXAMINED AND PASSED FOR ISSUE

(Primary Examiner) (Division)

NOTICE OF ALLOWANCE MAILED

FINAL FEE

Date	Amount

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BURGESS, DINKLAGE & SPRUNG
ATTORNEYS AT LAW
200 BROADWAY
NEW YORK 7, N.Y.

LOUIS BURGESS
RALPH D DINKLAGE
ARNOLD SPRUNG

EVELYN SOMMER
PETER J. FRANCO

CABLE "NYPATENT"
TEL. WORTH 8-3607

OCT 6 1962

October 15, 1962

Hon. Commissioner of Patents
Washington 25, D. C.

Re: Our File Metco 305.2

Sir:

In accordance with Rule 147 applicants wish to file a divisional application of:

Application S. N.	:	134 544
Filed	:	August 16, 1961
Applicants	:	Ferdinand J. Dittrich and Arthur P. Shepard
For	:	FLAME SPRAYING SYNERGISTIC COMPOSITES

This divisional application is to be directed to claims 1-23, 49, and 51-65 in connection with which restriction has been required.

Enclosed herewith is a filing fee check for $48.00 and the formal drawings required. The Office is requested to prepare a certified copy of application Serial No. 134 544 filed August 16, 1961, to serve as application papers and to charge the same to the account of the undersigned, account No. 02-4740.

Coff!

An amendment canceling the irrelevant claims is also enclosed herewith.

Respectfully,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

AS/k
Encls.

1/4

E 392

DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE

November 16, 1962
(Date)

THIS IS TO CERTIFY that the annexed is a true copy from the records of this office of the application of Ferdinand J. Dittrich and Arthur P. Shepard, as originally filed August 16, 1961, Serial Number 134,544, for Flame Spraying Synergistic Composites.

By authority of the
COMMISSIONER OF PATENTS

Certifying Officer.

D F 237786
E 393
APPLICATION BY
U.S. PATENT

FLAME SPRAYING SYNERGISTIC COMPOSITES

This invention relates to the flame spraying of synergistic composites. The invention more particularly relates to the flame spraying of synergistically-clad flame spray powders, to a novel group of flame spray materials comprising such synergistically-clad flame spray powders, and more broadly to the spraying of other synergistic composites wherein the synergistic action involves the generation of heat.

Flame spraying involves the feeding of a heat-fusible material into a heating zone, wherein the same is melted or at least heat-softened and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone formed by a flame of some type, where it is melted or at least heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by

sintering together finely divided material or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun, as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly produced from a flame caused by the combustion of a fuel, such as acetylene, propane, natural gas or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or in the newer type of guns, by a plasma flame. The plasma

flame may in itself constitute part of an electric arc or, in accordance with a newer development, may be in the form of a "free plasma stream", i.e., a stream of plasma which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead and zinc.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic or the like. While it is true that rods or wires formed from finely divided material bound together with a binder of plastic or the

like, as mentioned above, were known, the binder did not take part in the spraying or contribute to the coating and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form, which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spraying materials.

These and still further objects will become apparent from the following description read in conjunction with the drawings in which:

Fig. 1 diagrammatically shows a cross-section of a grain of a novel flame spray powder in accordance with the invention;

Fig. 2 is a diagrammatic cross-section of a further embodiment of a grain of a novel flame spray powder in accordance with the invention;

Fig. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray rod or wire in accordance with the invention; and

Fig. 4 shows an elevation of a further embodiment of a novel flame spray rod or wire in accordance with the invention.

In accordance with a broad aspect of the invention the flame spraying is effected with the material being sprayed in the form of a powder, the individual grains of which are in the form of a clad composite consisting of nuclei and at least one coating layer of a different material which will synergistically act with the nuclei in the process.

Each grain of the synergistically clad composite powders may also be in the form of a nucleus with two or more different coating layers which will synergistically act with each other and/or with the nucleus.

The synergistic action of the coating layer with the nucleus and the coating layers with each other, as the case may be, may manifest itself as a chemical or physical action or both, and may appear in the heating zone and/or along the path of travel to the surface to be coated, or at the sprayed coating as sprayed, or after a subsequent treatment such as a heating or fusing operation.

The synergistic action between the nuclei and/or the coating layer or layers may, for example, involve the physical or chemical generation of heat by exothermic reaction in the heating zone, along the path of travel to the target, or on the coated surface itself, so as to

increase the thermal efficiency of the process, aid in the bonding of the coating and/or produce results and effects by this in situ generated heat which cannot be achieved by the externally supplied heat. The synergism resulting in the exothermic reaction may be caused by the utilization of two components which will combine at the temperatures involved to form a material with a melting point higher than that of either of the constituents, with a considerable release of heat, by the use of components which will chemically combine in exothermic reaction, as for example where one acts as an oxidizing and the other a reducing agent, or by the use of components which will dissolve together in generation of heat or the like.

Thus, for example, one of the components may be a nickel-containing component and the other an aluminum-containing component which will combine under the spraying conditions to form a nickel-aluminum inter-metallic compound with an exothermic reaction. Similarly, one of the components may contain the aluminum and the other antimony, calcium, cobalt, lanthanum, lithium, manganese, nickel, palladium, praseodymium, dysprosium, or a combination thereof which, upon combining during the spraying, form a higher melting point compound with the generation of heat. Similarly the clad-composite powder may be a combination of nickel with elemental phosphorus, silver, copper, aluminum or the like, which will combine in exothermic reaction.

The synergistic action may also involve a protective effect of the coating material on the nuclei or a lower coating layer in order to prevent loss or destruction of this under-material and allow the spraying of the combination. Thus, for example, nickel may be coated on nickel-phosphorus, nickel-boron, or the like in order to prevent loss or destruction of the fluxing agent and allow the formation of a self-fluxing coating, as for example in the "spray-weld process."

The synergism may also involve a bonding effect in order to allow a satisfactory bonding on a base of sprayed materials which normally present bonding difficulties, as for example the synergism of a matrix metal, such as nickel or cobalt, with a hard or refractory material, such as tungsten carbide, Al_2O_3, diamonds or other hard gems or the like.

Bonding to the base or substrate being coated may also be aided by the synergistic action of exothermic reaction, as for example in the case of nickel-coated aluminum powder.

The synergistic effect may also involve the combining of the components to form a third component, such as a compound or alloy or inter-metallic compound desired as the coating constituent. This may involve a dissolving together of the components, alloying the components, or a chemical reaction between components which may be endothermic in nature if sufficient heat is available for the process.

The powder particles may be in the form of a nucleus with a single coating layer, or may be in the form of a nucleus with a multiple number of layers of the same or different materials.

The clad powders in accordance with the invention may be formed in any known or desired manner and preferably by the known chemical plating processes in which a coating material is deposited on a seed or nucleus of another material, or in which multiple layers of various materials are built up on the seed material, or in which various materials are co-deposited in a single layer on the seed material.

A preferred mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulphate on a seed powder catalyzed by the addition of anthraquinone. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor deposition, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal decomposition of halides, hydrides, carbonyls, organo-metals or other volatile compounds, or by displacement gas plating and the like.

The clad powders for this invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a

size between -60 mesh and 43 microns and preferably -140 and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the clad powders may be sprayed per se or in combination with other different clad powders, or in combination with other conventional flame spray powders or powder components.

Fig. 1 diagrammatically shows an embodiment of a clad powder having a nucleus of aluminum and a coating of nickel.

Fig. 2 shows a multi-layer powder of nickel and copper on nickel-boron.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder which decomposes in the heating zone of the gun, or, in certain cases the powders may be compacted and/or sintered together in the form of a rod or wire.

In the limited case where the synergistic action of the components involves an exothermic reaction as, for example, the combination of nickel and aluminum to form the nickel-aluminum inter-metallic compounds, the

spray material may assume a form other than the clad powder and may, for example, be in the form of a suitable aggregate or a composite wire, such as a wire having a coating sheath of one material, such as nickel, with a core of the other material, such as aluminum, as shown in Fig. 3, or wire formed by twisting together and rolling separate wires of components, such as nickel and aluminum, as shown in Fig. 4. Various combinations of other exothermically-reacting components may of course be used in the formation of such wire, which exothermic reaction will substantially contribute to the heat economy of the flame spraying and may even show self-ignition characteristics when fed through the spray gun.

The following examples are given by way of illustration and not limitation:

EXAMPLE 1

An aluminum powder having a particle size between -140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate, using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 300 and 350° F. in a mechanically agitated autoclave using solutions containing 40-50 grams per liter of nickel and 10-400 grams per liter of $(NH_4)_2SO_4$ and 20-30 grams

per liter of NH_3. About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i.g. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder is formed containing about 16 to 18% by weight aluminum and 84 to 82% by weight of nickel, and a size of -100 to +270 mesh.

The powder thus formed is flame-sprayed on a mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 7 inches from the plate, using a powder-type flame-spray gun as described in U. S. Patent 2,961,335, issuing November 22, 1960 and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermospray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel at a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu.ft./hr.

and oxygen as the oxidizing gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu.ft./hr.

The nickel coating and the aluminum base combine in the heat of the flame with a strong exothermic action, forming a nickel aluminum inter-metallic compound which deposits on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002" - .004" thickness is built up in this manner. The coating may be used as a base material for spraying of further layers of different metals or the like and serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .004" - .008", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020" - .040" or thicker as a wear-resistant - oxidation-resistant surface.

Due to its self-bonding characteristics the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the

powder has excellent oxidation-resistant characteristics even at high temperatures and in oxidising atmospheres, and will for example eliminate the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature, wear-resistant coatings.

When the example is repeated on a molybdenum rod of 3/16" diameter, with a coating between .008" - .010" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, with a welding torch, and cooled to room temperature with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10 - 45% by weight of aluminum and 55 - 90% by weight of nickel.

EXAMPLE 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough ground or light-grit-blasted; and titanium, rough-ground or light-grit-blasted.

In each case when a further material, such as steel, alumina or the like, was sprayed over the coating in the conventional and well known manner, the same was bonded with a tenacious bond, though if this material had been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

EXAMPLE 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface-cleaned by smooth grinding. Spraying is effected at a distance of about 7" from the plate at a rate of about 4 to 8

lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17 - 23 cu.ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29 - 33 cu.ft./hr.

A self-bonding cermet coating is formed which showed excellent thermal shock-resistance, hardness, abrasion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an increased amount of the inter-metallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

EXAMPLE 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium

zirconate spinel, ceria oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium silicide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

EXAMPLE 5

A nickel-phosphorus powder having a size between 200 and 325 mesh and containing 8 to 12% phosphorus is coated with nickel to form a composite-clad powder having a size between 140 and 270 mesh and containing 20 to 40% of the nickel phosphorus nucleus and 60 to 80% of the nickel coating.

The powder is sprayed in the identical manner described in Example 1. The coating obtained is mechanically bonded to the base and is slightly porous. This coating may be subsequently fused by a welding torch or furnace heated to form a homogenous pore-free coating welded to the base material.

EXAMPLE 6

A nickel-boron powder is coated with nickel to form a composite flame-spray

powder having a size between 120 and 325 mesh and containing 70 to 90% nickel, based on the nickel boron. The powder was sprayed in the manner described in Example 1 and a high quality of self-fluxing coating was formed.

The coating is mechanically bonded to the base and may be subsequently fused with a welding torch or in a furnace to form a dense homogenous, non-porous coating. When applied to a reactive base material, such as molybdenum, in a thickness of .006" to .010" or heavier, the coating can be fused to the base material by a torch or furnace without atmosphere control and below the recrystallization temperature of pure molybdenum, and will protect the molybdenum base from an oxidizing atmosphere at elevated temperatures up to the melting point of the nickel-boron coating.

EXAMPLE 7

Metallic cobalt is deposited as a coating on zirconia powder by the reduction of a cobalt ammonium sulphate solution with hydrogen so as to form a cobalt-clad zirconia flame-spray powder having a size between

140 mesh and 15 microns and containing 25 to 95% cobalt, based on the zirconia. The material is sprayed in the manner described in Example 1 on a grit-blasted base and a cermet coating is formed which shows excellent adhesion to the base and which will retard oxidation of the base. The coating furthermore has a high degree of hardness even at elevated temperatures, excellent shock-resistance and abrasion-resistance, and the metal matrix material is evenly distributed throughout the applied coating.

It is possible to vary the percentages of the ceramic in the composition between about 5 and 75% by weight in order to vary the properties of the coating. With an increased amount of ceramic in the cermet coating, the hardness and wear-resistant properties of the coating are correspondingly increased and the thermal conductivity decreased. Conversely, with an increasing amount of the cobalt matrix the bonding and shock-resistant properties are increased.

EXAMPLE 8

Al_2O_3 powder of a mesh size between 80 microns and 10 microns is coated with nickel in the manner described in Example 1 to produce a composite powder containing 25 to 95% of the nickel based on the aluminum oxide and having a particle size betsen 140 mesh and 15 microns. The powder is sprayed in the manner described in Example 1 on a grit-blasted base, and a cermet coating is formed which shows excellent adhesion to the base, a high degree of hardness even at elevated temperatures, and excellent thermal shock and abrasion-resistant characteristics. The metal matrix is evenly distributed throughout the sprayed coating.

In this case too it is possible to vary the percentage of the ceramic in the composite between 5 and 75% by weight, and with an increasing amount of ceramic, the hardness and wear-resistant properties increase, whereas with an increase of the nickel, the thermal conductivity, bonding and shock-resistant properties are increased.

EXAMPLE 9

Industrial diamond powder having a size between -120 and +140 mesh was coated with nickel in the manner described in Example 1 so that the nickel-clad composite powder formed contained about 25 to 30% by weight of the nickel, based on the diamonds. The powder was sprayed in the manner described in Example 1 on a steel base prepared by grit blasting, thus forming an excellent hone or lap in which the diamonds were firmly bonded in place.

EXAMPLE 10

Cobalt-bonded tungsten carbide particles of sharp, angular shape were coated with nickel in the manner described in Example 1, so as to produce a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 20 to 30% nickel based on the tungsten carbide. The powder was sprayed in the manner described in Example 9, with the formation of an excellent cutting hone or lap. The sharp angular edges of the initial tungsten carbide were retained in the coating.

Similar results were obtained when using

crystalline tungsten carbide in place of the cobalt bonded tungsten carbide particles.

EXAMPLE 11

A nucleus of elemental phosphorus powder was coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 80 to 98% nickel based on the phosphorus. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying phosphorus combines with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating which has self-fluxing properties.

EXAMPLE 12

A nickel boron powder is coated with copper and the copper-coated composite further coated with nickel to form a composite-clad flame spray powder having a particle size between 100 and 325 mesh containing 63 to 67% nickel and 26 to 32% copper and 2 to 10% boron by weight. The powder is sprayed in a powder-type flame spray gun on a lightly grit-blasted steel base with the flame spray gun

and method as described in Example 1. An excellent self-fluxing alloy is formed, which when fused in place by heating with an acetylene torch, forms a dense coating which corresponds in characteristics to monel.

EXAMPLE 13

A nickel boron powder is coated with chromium and the resulting coated powder in turn coated with nickel so as to form a flame spray composite-clad powder having a mesh size between 100 and 325 and containing 70 to 80% nickel and 18 to 20% chrome and 2 to 10% boron by weight. The powder is sprayed in the manner described in Example 12, resulting in a self-fluxing alloy coating which, when fused in place in the manner described in Example 12, produces a high grade coating having characteristics similar to nichrome V.

EXAMPLE 14

Nickel-bonded titanium carbide particles having a size between 140 and 325 mesh are coated with nickel, as described in Example 1, so as to produce a nickel-clad flame spray powder having a particle size between 100 and 270 mesh and containing 20 to 50% nickel based on the titanium carbide. The material

is sprayed in the manner described in Example 1 on a base with surface roughened by grit-blasting, and a high grade, bonded titanium carbide coating is formed in which the nickel acts as a matrix binding material.

When properly finished by grinding, the resultant coating is an excellent hard-facing, extremely resistant-to-wear coating even at elevated temperatures.

Similar results are obtained when using crystalline titanium carbide particles in place of the nickel-bonded titanium carbide particles.

EXAMPLE 15

Copper powder is coated with nickel in the manner described in Example 1 so as to form a nickel-clad composite flame spray powder having a particle size between 100 and 325 mesh and containing 60 to 70% nickel based on the copper. Upon spraying in the manner described in Example 1 on a base roughened by grit-blasting or other means, an excellent, corrosion and oxidation-resistant coating is formed. A similar coating is formed if the copper is replaced with chromium in an amount of 15 to 25% chromium based on the nickel.

EXAMPLE 16

Molybdenum disilicide powder is coated with nickel in the manner described in Example 1 so as to form a composite-clad flame spray powder having a particle size between 140 mesh and 10 microns, and containing 15 to 40% nickel by weight based on the disilicide. The powder is sprayed with the flame spray gun described in Example 1 on a base material roughened by grit-blasting.

The resultant oxidation-resistant coating is very dense, but may be further improved by subsequent heat treatment in a neutral to reducing atmosphere.

EXAMPLE 17

Example 10 is repeated except in place of the nickel, nickel phosphorus is used containing 4 to 12% of phosphorus. A similar coating resulted upon spraying, which however was self-fluxing.

EXAMPLE 18

Chromium boride powder is coated with nickel in the manner described in Example 1 so as to form a flame spray powder having a mesh size between 120 and 325 and containing 15 to 50% of nickel, based on the

chromium boride. Upon spraying in the manner described in Example 1, a boride coating of high quality is obtained which is resistant to wetting by molten metals.

Example 19

Silver solder powder is coated with nickel in the manner described in Example 1 so as to produce a nickel-clad composite powder having a size between 120 and 325 mesh and containing 25 to 50% nickel based on the silver solder. Upon spraying in the manner described in Example 1 on a base material prepared by grit-blasting, a low-fusing temperature, self-fluxing coating is formed which, when subsequently fused, is a homogenous, pore-free coating securely fused to the base material.

A simple mixture of powders consisting of 20 to 65% of this nickel-coated silver solder and 35 to 85% of a carbide (Example 10) is sprayed in the manner described in Example 1. The resultant coating, when fused, consists of angular carbide particles securely bonded to each other and to the base material.

The fused coating may be suitably finished by grinding for use as a wear-resisting coating or used, as fused, when the coated article is

to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

Example 20

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 50% nickel based on the titanium.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the nickel and titanium combine in the flame to form a corrosion-resistant coating.

Example 21

A niobium powder is coated with nickel in the manner described in Example 1 so as to form a composite nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 5 to 40% by weight of nickel based on the niobium.

The nickel protects the niobium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1 on a base material prepared by grit-blasting, the nickel and niobium combine in the flame to form a corrosion-resistant material.

EXAMPLE 22

A molybdenum powder was coated with nickel in the manner described in Example 1 so as to produce a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 5 to 40% nickel based on the molybdenum.

The nickel protects the molybdenum from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1 on a base material prepared by grit-blasting, the nickel and molybdenum combine in the flame to form a corrosion-resistant material.

EXAMPLE 23

A titanium boride powder was coated with nickel so as to form a flame spray powder having a particle size between 100 and 325 mesh and containing 20 to 50% nickel based on the titanium boride.

The nickel protects the titanium boride during the spray.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, a securely bonded nickel-titanium boride composite coating is achieved.

EXAMPLE 24

A silver powder is coated with nickel so as to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 30 to 70% nickel based on the silver.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the nickel and silver combine in the flame to produce a new material which is securely bonded to the base and is excellent for use as electrical contacts or the like.

During the spraying heat was evolved upon the combination of the nickel and silver, increasing the thermal economy of the process.

EXAMPLE 25

An aluminum powder is copper-plated so as to form a copper-clad flame spray powder having a particle size between 100 and 325 mesh and containing 85 to 98% or 8 to 20% copper based on the aluminum.

Upon spraying in the manner described in

Example 1, on a base material prepared by grit-blasting, the copper and aluminum combined in the flame to form a harder, corrosion-resistant alloy.

EXAMPLE 26

A silicon powder was coated with copper so as to form a copper-clad flame spray powder having a particle size between 100 and 325 mesh and containing 50 to 80% by weight of copper based on the silicon.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and silicon combine in the flame to form coatings of a material considerably more inert than copper.

EXAMPLE 27

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 50 to 80% copper based on the tellurium.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved

upon the combination of the copper and tellurium, increasing the thermal economy of the process.

EXAMPLE 23

Tin powder is coated with copper so as to form a copper-clad composite flame spray powder having a mesh size between 100 and 325 mesh and containing 75 to 95% copper based on the tin.

Upon spraying in the manner described in Example 1, upon a base material prepared by grit-blasting, the copper and tin combined in the flame to produce a ductile, corrosion-resistant coating.

EXAMPLE 24

Lead powder is coated with copper so as to form composite flame spray powder having a particle size between 100 and 325 mesh and containing 50 to 90% copper based on the lead.

Upon spraying in the manner described in Example 1, upon a base material prepared by grit-blasting, an excellent, leaded copper material is deposited which is suitable for use as a bearing.

EXAMPLE 25

The nickel-clad flame spray powder of Example 1 is mixed with about 20% by weight

of low pressure polyethylene powder and rolled at a temperature of about 212° F. into the form of a rod of 1/3" diameter. The rod is sprayed, using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4E Gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as oxidizing gas at a pressure of 35 p.s.i. and a flow rate of 75 cu.ft./hr; with air as a blast gas at a pressure of 40 p.s.i. and a flow rate of 25 cu.ft./min. The end coating produced is similar to the coating produced in Example 1.

Example 11

The nickel-clad flame spray powder of Example 10 is compacted and sintered in the form of a rod .125" in diameter. The rod is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. as the Metco-type 4E Gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as the oxidizing gas at a pressure of 35 p.s.i. and a flow rate of 75 cu.ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu.ft./min. The end coating produced is similar to the coating produced in Example 10.

Example 32

A wire is formed by encasing a core of aluminum in a tube of nickel and drawing to a size of .125" in diameter plus or minus .002. The wire contains 82 to 84% by weight of nickel based on the aluminum.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4E Gun. Spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as the oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu.ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu.ft./min. After initiation of the exothermic combination reaction at the melting wire tip, the flow of fuel and oxidizing gas may be drastically reduced, thus utilizing the heat of reaction to aid in melting the spray material and contributing to the over-all economy of the process. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55 - 90% by weight of nickel in the wire.

Example 33

A composite wire is formed by winding individual wires of nickel and aluminum and drawing the same to a thickness of .125" plus or minus .002". The wire contains 82 to 84% by weight of nickel based on the aluminum. The wire is sprayed in the manner described in Example 32, with identical conditions and coating resulting.

Example 34

A self-fluxing silver-solder powder containing 15% silver, 5% phosphorus and 80% copper, is coated with copper so as to form a composite flame spray powder having a particle size between 100 and 325 mesh and containing 20 to 50% copper based on the silver-solder.

Upon spraying in the manner described in Example 1, on a base material prepared by light grit-blasting, an excellent, low melting point, self-fluxing alloy is deposited.

Example 35

Example 34 is repeated except nickel is used in place of the copper. Similar results are obtained.

EXAMPLE 35

A simple mixture of powders containing 10 to 25% of the composite nickel - nickel phosphorus powder described in Example 5 and 75 to 90% of copper or copper alloy powder of the kind known as "Everdur" is sprayed with the gun and spray conditions described in Example 1.

The coating as described is mechanically bonded to the base material and slightly porous by nature. It may be subsequently fused by torch or furnace heating to form a homogenous, pore-free coating welded to the base material. After fusion the coating is a fairly hard, corrosion-resistant, welded bronze overlay.

EXAMPLE 37

Example 36 is repeated, using, however, the composite nickel - phosphorus powder described in Example 11 in place of the nickel - nickel phosphorus powder.

Comparable results are obtained.

EXAMPLE 38

A simple mixture of powders containing 69% of the composite powder as described in Example 6 and 31% pure copper powder in the particle size range -140 and +325 mesh is sprayed with the gun as described in Example 1.

The coating as applied may be

subsequently fused without atmosphere control, to form a homogenous alloy fused to the base material, which corresponds in characteristics to monel.

EXAMPLE 39

A simple mixture of powders containing 81% of the composite powder as described in Example 6 and 19% of pure chromium powder in the particle size range -140 and +325 mesh is sprayed with the gun as described in Example 1.

The coating as applied may be subsequently fused without atmosphere control, to form a homogenous alloy fused to the base material, which corresponds in characteristics to Nichrome V.

EXAMPLE 40

Example 9 is repeated except in place of the nickel, nickel phosphorus was used containing 6 to 12% of phosphorus. A similar coating resulted upon spraying, which however was self-fluxing. Fusion bonding of particles to each other and to the base was accomplished by fusing the applied coating.

EXAMPLE 41

The coated diamond powder of Example 9 is mixed with nickel-coated silver solder powder

of Example 19 in the proportion of 50 to 75% diamond to 25 to 50% matrix material.

The mixture was sprayed in the manner described in Example 1 and the deposit subsequently fused.

The resultant coating was a dense, pore-free coating fused to the base material in which the diamonds were securely anchored by the low melting point, self-fluxing matrix metal.

EXAMPLE 42

Example 14 is repeated except in place of the nickel, nickel phosphorus is used containing 4 to 12% of phosphorus. A similar coating resulted which, however, was self-fluxing.

EXAMPLE 43

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared

by light grit-blasting, in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

EXAMPLE 44

A molybdenum powder having a particle size range between 140 and [illegible] mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type M3 Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of

11.5 cu. ft./hr., using a No. 3 (pointed) electrode and No. 3R Argon nozzle, and using arc current of 550 amperes at 45 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 45

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

EXAMPLE 46

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 3M Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder perhour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 11.5 cu. ft./hr., using a No. 3 (pointed) electrode and No. 3R Argon nozzle, and using arc current of 550 amperes at 45 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 47

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 47% zirconium and 53% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

EXAMPLE 48

A titanium powder having a particle size range between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 35% chromium and 65% titanium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the titanium base combine in the heat of the flame, forming a chromium titanium inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

EXAMPLE 49

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a

powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 11.5 cu. ft./hr., using a No. 3 (pointed) electrode and No. 3R Argon nozzle, and using arc current of 550 amperes at 45 volts.

The titanium base and silicon coating combine in the heat of the flame, forming a titanium silicon inter-metallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 50

A dysprosium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum inter-metallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 51

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum inter-metallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 52

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in

Example 1.

The aluminum coating and the chromium base combine in the heat of the flame with a strong exothermic action, forming a chromium aluminum inter-metallic compound which deposits on the base as a dense, high quality coating of very high melting point and excellent oxidation-resistance.

EXAMPLE 53

Example 52 is repeated except that the composite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

EXAMPLE 54

The nickel-clad aluminum composite powder of Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of -140 mesh +10 microns, and preferably -140 +325 mesh in proportions of:

a) 80 weight percent tungsten carbide to 20 weight percent of the composite,

b) 20 weight percent of the carbide to 80 weight percent of the composite, and

c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface cleaned by grinding or very light sand-blast cleaning. The spraying is effected at about 8-9 inches from the plate, using a powder-type flame-spray gun as described in U.S. patent 2,961,335, issuing November 22, 1960, and sold by Metco, Inc. of Westbury, Long Island, New York under the tradename of "Thermo-Spray" powder gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 psi and a flow rate of 20 to 30 cubic feet per hour and oxygen as the oxidizing gas at a pressure of 14 psi and a flow rate of 30 to 40 cubic feet per hour.

The nickel-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on impact with the substrate, becomes the matrix which securely binds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by proper grinding procedure, the resultant coating is of a highly wear-resistant coating material, applicable to virtually any base material and not subject to the limitations

of the previously used self-fluxing alloy matrix materials which must be fused at approximately 1900°F.

EXAMPLE 55

Example 54 is repeated except that in place of the grade of tungsten carbide cobalt powder grains used, cobalt-bonded tungsten carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 54. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resisting coating or used as deposited where the coated article is to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

EXAMPLE 56

Example 55 is repeated except that in place of the cobalt-bonded tungsten carbide grains described, the nickel-clad tungsten carbide grains described in Example 10 were substituted.

EXAMPLE 57

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 54. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means is a highly wear-resistant, hard coating.

EXAMPLE 58

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 54. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished by grinding or other means presents a highly wear-resistant, hard surface.

EXAMPLE 59

Example 54 is repeated except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium carbide, chromium carbide and mixtures of the various carbides are used.

EXAMPLE 60

The nickel-clad aluminum core composite from Example 54 is mixed with aluminum powder in the mesh size range -100 +325 mesh, and preferably in the -170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 54. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat treating in the temperature range 1250°F. to 1500°F. in reducing atmosphere, dry hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogenous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt water corrosion.

EXAMPLE 61

The nickel-clad aluminum composite powder of Example 34 is mixed with Monel powder of a size between -100 mesh and 410 microns, and preferably between -140 and +325 mesh in the proportions 35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 34. The resultant coating is self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, considerably increase the particle to particle bonds within the coating and decrease the permeability of the coating.

EXAMPLE 62

Example 61 is repeated except that nickel and stainless steel powders are substituted for the Monel.

EXAMPLE 63

Example 61 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished by grinding or other means shows high resistance

to abrasion, wear, and galling by other metals, and is an excellent bearing surface.

As may be noted from the foregoing the flame spraying of synergistically-acting composites in accordance with the invention is effected in the conventional manner, using the conventional flame spray equipment and utilizing conventional surface-preperation, though in certain instances wherein the spray coating has self-bonding characteristics, special surface-preparation other than a good cleaning, is not critical.

The synergistic composites in accordance with the invention may be sprayed in conjunction with or in addition to other flame-spray materials conventionally used in the art, or may be sprayed in combination with or conjunction with each other. Thus the synergistically clad powders in accordance with the invention may be sprayed in admixture with other conventional spray powders or mixtures of two or more of the composite powders in accordance with the invention. may be sprayed.

In case of powders comprised of synergistically clad particles the components of which exothermically react forming an inter-metallic compound, the spraying in admixture with other composites or with other conventional spray materials offers many advantages.

The use of these composite powders, such as nickel-coated aluminum particles, will generally improve

the bond of the total sprayed mixture and thus of the other component or components to the substrate making the mixture self-bonding. The porosity bond will also be improved so that the porosity of the coating may be decreased. The use of the composites in admixture with conventional spray powders may thus be used to improve the characteristics and properties of the materials or, conversely, the properties of the composites, such as the nickel-aluminum deposits may be enhanced or other new or better properties may be obtained.

In general as little as 20% by weight of the composite containing exothermically reacting components will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame-spray powders such as conventional metal or alloy powders. There is, of course, no upper limit on the amount of the composites may be sprayed per se, but generally about 20% by weight of the other component is required in order to have a pronounced effect on the characteristics of the coating. Thus, for example, using a mixture of a nickel clad aluminum powder as for instance, is shown in Example 1, with tungsten carbide, titanium carbide, tantalum carbide, chromium carbide, molybdenum, niobium and tantalum amounts of 20% to 80%, and preferably 25% to 50% by weight of the composite may be used. The mixtures are self-bonding as sprayed and form abrasion and wear-resistant coatings. When the same composite is sprayed in mixture with Monel, stainless steel, nickel, chromium, etc., amounts of 25% to 75% by weight of the composite, and

preferably 30% to 40% by weight of the composite are used. When sprayed in admixture with aluminum as little as 5% of the aluminum will vary the characteristics of the coating, though preferably up to 25% of the aluminum is used. The composite as mentioned may also be sprayed in admixture with iron, nickel or nichrome or produce a self-bonding mixture which produces a coating of lower permeability. It is of course, impractical to list all of the materials which may be sprayed in conjunction or admixture with the composites in accordance with the invention, but the selection of such materials for specific purposes is within the skill of the artisan in light of the disclosure.

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention is therefore only intended to be limited by the appended claims or their equivalents wherein we have endeavored to claim all inherent novelty.

This application is a continuation-in-part of our copending application Serial No. 72 543, filed November 22, 1960.

We claim:

1. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of individual, synergistically clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and synergistically acting with the said nucleus in the process.

2. Improvement according to claim 1 in which said nucleus and said coating layer are of materials exothermically reacting with each other at the temperature developed in said heating zone.

3. Improvement according to claim 1 in which said coating layer comprises a bonding agent for said nucleus.

4. Improvement according to claim 1 in which said nucleus contains a self-fluxing material.

5. Improvement according to claim 1 in which said nucleus comprises a refractory material and in which said coating comprises a bonding matrix for said nucleus.

6. Improvement according to claim 1 in which said coating layer comprises nickel and in which said nucleus is a member selected from the group consisting of aluminum, nickel-phosphorus, nickel-boron, phosphorus-copper, chromium, silver solder, and silver.

7. Improvement according to claim 6 in which said coating material is nickel and in which said nucleus contains aluminum, said aluminum being present in amounts of about 10 to 45% based on the nickel.

8. Improvement according to claim 1 in which said coating layer is nickel and said nucleus a refractory material.

9. Improvement according to claim 1 in which said coating layer is nickel and said nucleus is a carbide.

10. Improvement according to claim 9 in which said carbide is tungsten carbide.

11. Improvement according to claim 1 in which said coating layer is nickel and in which said nucleus is aluminum oxide.

12. Improvement according to claim 1 in which said coating layer is nickel and said nucleus is diamond.

13. Improvement according to claim 1 in which said coating layer is nickel and said nucleus contains aluminum, and in which said synergistically clad particles are passed into said heating zone in admixture with a refractory oxide powder.

14. Improvement according to claim 13 in which said refractory oxide is aluminum oxide.

15. Improvement according to claim 1 in which said coating layer is cobalt and said nucleus is zirconia.

16. Improvement according to claim 2 in which said coating layer is copper and in which said nucleus comprises a member selected from the group consisting of tin, lead, and aluminum.

17. Improvement according to claim 1 in which one of said coating layer and said nucleus comprises silicon and the other a member selected from the group consisting of molybdenum, chromium, aluminum and titanium.

18. Improvement according to claim 1 in which one of said coating layer and said nucleus comprises chromium and the other a member selected from the group consisting of silicon, zirconium, titanium and aluminum.

19. Improvement according to claim 1 in which one of said coating layer and said nucleus comprises aluminum and the other a member selected from the group consisting of dysprosium, lantharum and chromium.

20. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite comprising at least two exothermically reacting components.

21. Improvement according to claim 20 in which said heat-fusible material is in the form of a wire.

22. Improvement according to claim 21 in which one component of said composite comprises nickel and the other aluminum.

23. Improvement according to claim 22 in which said wire has an aluminum core and nickel covering.

24. A flame spray powder in the form of individual, synergistically clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and synergistically active with said nucleus in flame spraying.

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25. A flame spray powder according to claim 24 in which said nucleus and said coating layer are of exothermically reacting materials.

26. A flame spray powder according to claim 24 in which said coating layer comprises a bonding agent for said nucleus.

27. A flame spray powder according to claim 24 in which said nucleus contains a self-fluxing material.

28. A flame spray powder according to claim 24 in which said nucleus comprises a refractory material and said coating comprises a bonding matrix for the material of said nucleus.

29. A flame spray powder according to claim 24 in which said coating layer comprises nickel and in which said nucleus is a member selected from the group consisting of aluminum, nickel-phosphorus, nickel-boron, phosphorus-copper, chromium, silver solder, and silver.

30. A flame spray powder according to claim 24 in which said coating material is nickel and in which said nucleus contains aluminum, said aluminum being present in amounts of about 10 to 45% based on the nickel.

31. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus is a refractory material.

32. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus is a carbide.

33. A flame spray powder according to claim 32 in which said carbide is tungsten carbide.

34. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus is aluminum oxide.

35. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus is diamond.

36. A flame spray powder according to claim 24 in which said coating layer is nickel and said nucleus contains aluminum, and in which said powder is in admixture with a refractory oxide powder.

37. A flame spray powder according to claim 24 in which said refractory oxide powder is aluminum oxide powder.

38. A flame spray powder according to claim 24 in which said coating layer is cobalt and said nucleus is zirconia.

39. A flame spray powder according to claim 24 in which said coating layer is copper and said nucleus comprises a member selected from the group consisting of tin, lead and aluminum.

40. A flame spray powder according to claim 24 in which said powder is bonded in the form of a wire.

41. A flame spray powder according to claim 24 in which one of said coating layer and said nucleus comprises silicon and the other a member selected from the group consisting of molybdenum, chromium, aluminum and titanium.

42. A flame spray powder according to claim 24 in which one of said coating layer and said nucleus comprises chromium and the other a member selected from the group consisting of silicon, zirconium, titanium and aluminum.

43. A flame spray powder according to claim 24 in which one of said coating layer and said nucleus comprises aluminum and the other a member selected from the group consisting of dysprosium, lanthanum and chromium.

44. A flame spray powder according to claim 24 including at least one additional coating layer differing from said nucleus and first mentioned coating layer and synergistically active with at least one of said nucleus and first mentioned coating layer in

45. A flame spray material in the form of a composite comprising at least two exothermically reacting components in intimate contact with each other.

46. A flame spray wire containing at least two exothermically reacting components in intimate contact with each other.

47. A flame spray wire according to claim 46 in which one of said components comprises nickel and the other aluminum.

48. A flame spray wire according to claim 47 in which said wire has an aluminum core and nickel covering.

49. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of individual, synergistically clad particles comprising a nucleus and at least two coating layers of materials differing from each other and synergistically acting with each other in the process.

50. A flame spray powder in the form of individual, synergistically clad particles comprising a nucleus and at least two separate coating layers of material differing from each other and synergistically active with each other in flame spraying.

51. In the flame spraying process in which a heat-fusible material is sprayed onto a base, the improvement to increase the bond which comprises spraying an intermediate layer of two components exothermically reacting with each other, forming an inter-metallic compound.

52. Improvement according to claim 51 in which one of said components comprises nickel and the other aluminum.

53. Improvement according to claim 51 in which one of said components comprises chromium and the other aluminum.

54. A base having a flame spray coating bonded in place by an intermediate bonding layer of an inter-metallic compound formed from two exothermically reacting components.

55. An article according to claim 54 in which said inter-metallic compound is a nickel aluminum inter-metallic compound.

56. An article according to claim 54 in which said inter-metallic compound is a chromium aluminum inter-metallic compound.

57. A base having a flame sprayed coating of an inter-metallic compound formed of two exothermically reacting components.

58. A coated base according to claim 57 in which said inter-metallic compound is a nickel aluminum inter-metallic compound.

59. A coated base according to claim 57 in which said inter-metallic compound is a chromium aluminum inter-metallic compound.

60. A base having a flame sprayed coating produced by the process according to claim 1.

61. A base having a flame sprayed coating produced by the process according to claim 49.

62. Improvement according to claim 6 in which said coating material is nickel and in which said nucleus contains aluminum, said aluminum being present in amounts of about 16 to 13% based on the nickel.

63. Improvement according to claim 1 in which said synergistically clad particles are passed into said heating zone in admixture with another heat-fusible material.

64. Improvement according to claim 63 in which said nucleus and said coating layer are of materials exothermically reacting with each other at the temperature developed in said h[illegible] zone forming an inter-metallic compound.

65. Improvement according to claim 64 in which said coating material is nickel and in which said nucleus contains aluminum, said aluminum being present in amounts of about 10 to 45% based on the nickel.

66. Flame spray powder according to claim 24 in which said nucleus and said coating layer are of materials which will exothermically react when heated to form an inter-metallic compound and in which said powder is in admixture with another flame spray powder.

67. Flame spray powder according to claim 66 in which said coating material is nickel and in which said nucleus contains aluminum in amounts of about 10 to 40% based on the nickel.

Meteo 305.1

E 456

OATH, POWER OF ATTORNEY AND PETITION

Being duly sworn, we, Ferdinand J. Dittrich and Arthur P. Shepard, residing at 2457 New Place, Bellmore, Long Island, New York and 29-01 - 159th Street Flushing, Long Island, New York, respectively, depose and say that we are citizens of the United States; that we have read the foregoing specification and claims and we verily believe that we are the original, first and joint inventors of the invention or discovery of FLAME SPRAYED SYNEMOISTIC COMPOSITES described therein; that this application discloses and claims subject matter disclosed in our pending application U. S. Serial No. 72,543, filed November 22, 1960 that as to the subject matter of this application which is common to said application we do not know and do not believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than one year prior to said application, or in public use or on sale in the United States for more than one year prior to said application; that said common subject matter has not been patented before the date of said application in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months prior to said application; that as to the subject matter of this application which is not common to said application we do not know and do not believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than

one year prior to this application or in public use or on sale in the United States for more than one year prior to this application, and that said subject matter has not been patented in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months prior to this application; and that no application for patent on said invention has been filed by us or our representatives or assigns in any country foreign to the United States.

And we hereby appoint BURGESS, DINKLAGE & SPRUNG (Registration No. 15,379), a firm composed of Ralph D. Dinklage and Arnold Sprung, of 233 Broadway, New York 7, New York our attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith.

WHEREFORE, we pray that Letters Patent be granted to us for the invention or discovery described and claimed in the foregoing specification and claims, and we hereby subscribe our names to the foregoing specification and claims, oath, power of attorney, and this petition, this 7th day of May, 1961.

Inventor: Ferdinand J. Dittrich

2457 New Place, Bellmore, Long Island, New York

Inventor: Arthur P. Shepard

29-01 159th Street, Flushing, Long Island, N. Y.

State of New York
County of Nassau } ss.

Before me personally appeared Ferdinand J. Dittrich and Arthur P. Shepard, to me known to be the persons described

in the above application for patent, who signed the foregoing instrument in my presence, and made oath before me to the allegations set forth therein as being under oath, on the day and year aforesaid.

John J. Brennan

JOHN J. BRENNAN
Notary Public, State of New York
No. 30-[illegible]
Qualified in Nassau County
Commission Expires [illegible], 1962

L.A.

237780 DIV. 25

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E 459.

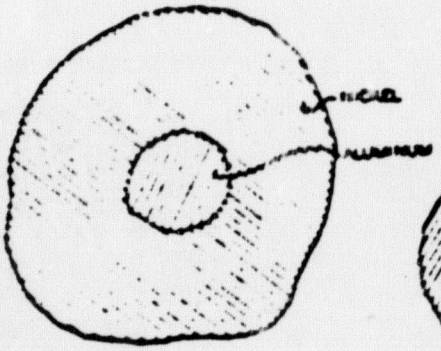

Fig 1

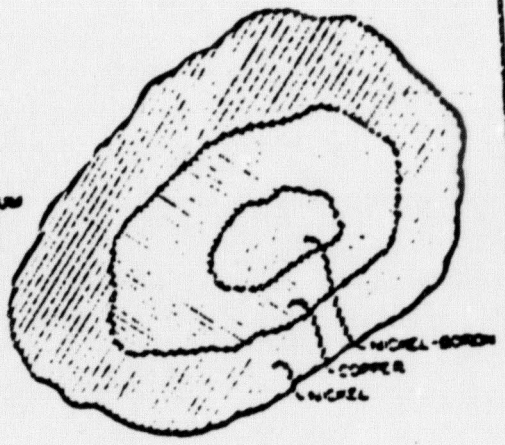

Fig 2

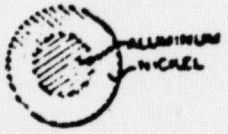

Fig 3

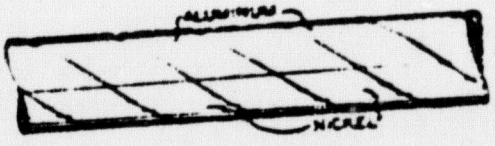

Fig 4

INVENTORS
FERDINAND J. DITTRICH
ARTHUR P. SHEPARD
BY
Larson, Taylor & Hinkley
ATTORNEYS

45

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AS/k

IN THE UNITED STATES PATENT OFFICE

237786

Amendment in Divisional Application of

Application Serial No. : 134 544

Applicants : Ferdinand J. Dittrich and Arthur P. Shepard

Div.25

Filed : August 16, 1961

For : FLAME SPRAYING SYNERGISTIC COMPOSITES

October 15, 1962

Hon. Commissioner of Patents
Washington 25, D. C.

AMENDMENT CANCELING IRRELEVANT CLAIMS

Sir:

Kindly cancel claims 24-48, 50, 66 and 67.

REMARKS

The claims elected for further prosecution in parent application Serial No. 134 544 are hereby cancelled.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

E 461

OCT 24 1962

Burgess, Dinklage & Sprung
233 Broadway
New York 7, New York

Gentlemen:

On Oct. 16, 1962, this Office received from you a fee of forty-eight dollars, 1 sheet of drawing, an order for a certified copy of the parent application as filed and a proposed amendment in an application in the name of Ferdinand J. Dittrich and Arthur F. Shepard, for Plano Spraying Apparatus Comprising, as a division of application Serial Number 134,[illegible], under the provisions of Rule 147.

After entry of the proposed amendment, the divisional application would contain a total of 39 claims, requiring a filing fee of $47. Upon receipt of $1.00 to cover the balance of the filing fee, the certified copy of the application will be prepared and the application given a filing date of the date on which the balance filing fee is received in this Office.

Sincerely yours,

R. L. RUDELSHEIM
ASST. HEAD OF THE
APPLICATION BRANCH

yas

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RECEIVED
OCT 26 1962
U.S. PATENT OFFICE

100-107-A

E 462

BURGESS, DINKLAGE & SPRUNG
ATTORNEYS AT LAW
200 BROADWAY
NEW YORK 7, N. Y.

LOUIS BURGESS
RALPH D DINKLAGE
ARNOLD SPRUNG

EVELYN SOMMER
PETER J FRANCO

CABLE "NYPATENT"
TEL. WORTH 2-3607

October 25, 1962

237786

Hon. Commissioner of Patents
Washington 25, D. C.

Re: Our File Metco 305.2

Attention: Mr. R. J. Rosenbaum
Asst. Head of the Application Branch

Sir:

With reference to your letter of October 24, 1962 copy of which is attached hereto for your convenience, we enclose herewith our check for $1.00.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By:

AS/k
Encls.

E 463

NOV 2 1962

Burgess, Dinklage & Sprung
233 Broadway
New York 7, New York

Gentlemen:

On Oct. 26, 1962, this Office received from you the balance filing fee of $1.00 in an application in the names of Ferdinand J. Litterick and Arthur F. Shepard, for Plane Spraying Synergistic Compositions, as a division of application Serial No. 134, 544, under the provisions of Rule 147.

In view of this, the Office will prepare the certified copy of Serial Number 134,544 in compliance with your request and the divisional application given a filing date of Oct. 26, 1962, and a Serial Number. The filing receipt will be mailed to you in the course of business.

Sincerely yours,

[illegible]
[illegible]
APPLICATION BRANCH

yas

69

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 464

In Reply Please Refer To

Burgess, Dinklage & Sprung
233 Broadway
New York 7, New York

Applicant: Ferdinand J. Dittrich et al.	
Ser. No. 237,786	
Filed Oct. 26, 1962	OCT 30 1964
For FLAME SPRAYING SYNERGISTIC COMPOSITE	GROUP 160

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

SHORTENED TIME FOR REPLY

This application has been examined.

References applied:

Mackiw et al.	2,853,403	Sept. 23, 1958	117-100M
White et al.	2,976,166 (Filed May 5, 1958)	Mar. 21, 1961	117-46FS
Boggs	2,988,807 (Filed May 29, 1959)	June 20, 1961	117-46FS
Shwayder	3,049,435 (Filed Aug. 19, 1957)	Aug. 14, 1962	117-22
Bayer	3,050,409 (Filed Nov. 30, 1959)	Aug. 21, 1962	117-22
Joseph	3,102,044 (Filed Sept. 12, 1960)	Aug. 27, 1963	117-22

Art cited of interest:

Harshaw	1,986,197	Jan. 1, 1935	29-192 CPM
Bleakley	2,231,247	Feb. 1, 1941	117-105
Hensel et al.	2,370,242	Feb. 27, 1945	117-100M
Cole	2,694,647	Nov. 16, 1954	117-22
Wheildon	2,707,691	May 3, 1955	117-105.2
Montgomery	2,775,531	Dec. 25, 1956	117-22
Shepard	2,936,229	May 10, 1960	75-0.55

70 12

Alexander et al.	2,949,358 (Filed Sept. 23, 1960)	Aug. 16, 1960	75-176
Peerman et al.	2,964,420 (Filed June 14, 1955)	Dec. 13, 1960	117-105.2X
Strate	2,996,322 (Filed Dec. 31, 1957)	Aug. 29, 1961	117-22
Stephenson	3,015,880 (Filed Nov. 6, 1958)	Jan. 9, 1962	117-46 FS
Schrewelius	3,025,182 (Filed Mar. 3, 1958)	Mar. 13, 1962	117-105
Pelten et al.	3,071,489 (Filed May 28, 1958)	Jan. 1, 1962	117-46 FS
Reed	3,117,845 (Filed Apr. 27, 1960)	Jan. 14, 1964	117-22X

Edwards et al., Aluminum Industry, Vol. 2, 1930 Mc Graw Hill Book Co., (pp. 108-114 relied on)

Claims 1, 3 to 5 and 8 to 10 are rejected as unpatentable over Shwayder under 35 U.S.C. 102. This patent teaches flame spraying of Tungsten carbide particles coated with nickel or nickel phosphide.

Claims 2, 6 and 11 to 15 and 21 are rejected as unpatentable over Shwayder in view of either White or Bayer under 35 U.S.C. 103. The Shwayder reference has been discussed in the previous paragraph. The White and Boyer patents disclose the conventional Thermit process wherein a metal oxide and a metal mixture react exothermally as in flame spraying. It would be obvious to one skilled in the art to employ any materials in flame spraying and employ coated particles rather than a mixture as taught by Shwayder. No unexpected results are obtained.

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Claim 16 is rejected as unpatentable over Boggs in view of Shwayder under 35 U.S.C. 103. Boggs discloses flame spraying of a copper-aluminum mixture. It would be obvious to one skilled in the art to employ coated particles in flame spraying as taught by Shwayder in the teachings of Boggs.

Claims 7 and 17 to 19 are rejected as unpatentable over Shwayder in view of either Joseph or Mackiw et al. under 35 U.S.C. 103. The Shwayder patent has been previously discussed. The Joseph and Mackiw et al. references both disclose powdered material that is applied to a base by spraying. It would be obvious to one skilled in the art to employ any coated particulate metal or refractory material in the basic reference of Shwayder.

Claims 20 and 21 are rejected as unpatentable over either White or Bayer under 35 U.S.C. 102. These patents discloses the conventional Thermit process wherein two coating materials react exothermally.

Claims 22 and 23 are rejected as unpatentable over either White or Bayer in view of Mackiw et al. under 35 U.S.C. 103. The White, Bayer and Mackiw et al. references have been previously discussed. It would be obvious to one skilled in the art to employ the material of Mackiw et al. in the process of White or Bayer.

Claims 49 and 51 to 53 are rejected aon the references, and for the reasons applied in the previous paragraph. It would be obvious to one skilled in the art to employ

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multiple coating layers, and use conventional materials as taught by the references applied.

Claims 54, 57, 63 and 64 are rejected as fully met by White or Bayer.

Claims 55, 56, 58, 59, 61, 62 and 65 are rejected as unpatentable over either White or Bayer, in view of Mackiw under 35 U.S.C. 103. The articles produced are obvious from the references applied. The particular percentages of materials employed is seen to be a mere matter of choice.

Claims 60 and 63 are rejected as unpatentable over Shwayder under 35 U.S.C. 102. The article product by applicant's process reads on the article of Shwayder.

The Marshaw, Hensel et al., Alexander et al., Poorman et al. and Cole references have been cited of interest since they teach the employment of particulate material. The Bleakley, Strate, Wheilden Jr., Montgomery et al., Shepard, Stephenson, Schrewelius, Reed and Pelton references have been cited since they teach various techniques in flame spraying. The Edwards et al. publication shows various alloys of aluminum.

Summary:

Claims rejected: 1 to 23, 49 and 51 to 65.

Claims allowed: none.

Attention is directed to the Commissioner's address published in 803 O.G. 893.

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE FOUR MONTHS FROM THE DATE HEREOF.

Abandoned 11/3 11, 5

R. D. Nairus
Examiner

A.Golian:meb
WO 7-2525

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E 469 F2 Metco 305.2

MAIL ROOM NOV 23 1964 U.S. PATENT

RECEIVED NOV 25 1964

IN THE UNITED STATES PATENT OFFICE

GROUP 16

Applicants: Ferdinand J. Dittrich et al.

Serial No.: 237,786

Filed : October 26, 1962

For : FLAME SPRAYING SYNERGISTIC COMPOSITES Group 160

November 20, 1964

Hon. Commissioner of Patents
Washington 25, D.C.

Sir:

BURGESS, DINKLAGE & SPRUNG, attorneys of record in the above entitled application, announce their change of address as of April 30, 1964 to 605 Third Avenue, New York City, N.Y. 10016, and respectfully request that all future correspondence and actions be addressed to them at that address.

Very truly yours,

BURGESS, DINKLAGE & SPRUNG

By _____
Attorneys for Applicants

75

ATTORNEY'S ROOM

E 470 #6

MAR 1 6 1968

U. S. PATENT OFFICE

Hon Comours of Patents:

Your petitioner requests access to the file of abandoned application Serial No. 237,786 filed Oct 26, 1962 and referred to in U S Patent 3822515

Steven Goldby
3/12/68

APPROVED
MAR 12 1968

ATTORNEY'S ROOM

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E 471

April 22, 1968

Hon. Commissioner of Patents

Washington, D. C. 20231

S I R :

PETITION FOR ACCESS

The undersigned hereby petitions for access to the file of abandoned application Serial No. 237,786 filed October 26, 1962.

Access to this application file is necessary in order to determine the scope and validity of the claims of the issued patent.

This application is mentioned in U. S. patent 3,322,515, issued May 30, 1967.

Respectfully,

SHOEMAKER AND MATTARE

By John F. Smith

approved
4/24/68
J. F. Plummer

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E 472

INDEX OF CLAIMS

237786

U. S. PATENT OFFICE

DEC 10 1962

SEARCHED

Class	Sub	Date	Exr
117	105.2		
	106.5		
	100 M		
	I		
29	191		
	193		
	194		
75	0.55		
117	71		
	30		
	105	10/64	ABS

Claims		Date		Claims		Date	
Final	Original			Final	Original		

SYMBOLS

STATUS

23778

E 473

CONTENTS

1. Application ✓ papers.
2. Print Nov 27 1962
3. Use Condt Ltr Oct 16 1962
4. REJECTION OCT 30 1964
5. Chg. of Address Dec. 23, 1964
6. Request for Access 3-2-65
7. Request for Access April 20, 1965
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Form PO-436a (1-1-58)

343705	P. R. Div.		PATENT NUMBER
Assistant examiner	Class	Subclass	DATED
Division No. 110/160	Filed complete (Date) FEB. 10, 1964	Serial No. 343 705	CLAIMS FOREIGN PRIORITY: Country / Date
Number claims allowed	Print claim(s)	Class	Subclass

Applicant(s)

DIETRICH, FERDINAND J. OF BELLMORE, L. I., N. Y. AND SHEPARD, ARTHUR P. OF FLUSHING, L. I., N. Y.

Assignor(s) to

Title of invention

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

☐ Division of ☐ Continuation of ☐ Substitute for abandoned ☒ Continuation-in-part of

APPLICATION Serial No.	Filed	APPLICATION Serial No.
		(1) 75,343
		(2) 134,574
		787,266
Now Patent No.	Granted	Filed Dec. 22, 1960
		Aug. 16, 1961
		Oct. 26, 1962

Sh. drw.	Extra claims	Filing fee	Transaction	Atty's docket
1	38	$68	69288	METCO 305.3

Send correspondence to:

BURGESS, DINKLAGE & SPRUNG
~~233 BROADWAY~~ 535 Fifth Ave.
NEW YORK ~~7~~, N. Y. 10016

Principal attorney(s)

BURGESS, DINKLAGE & SPRUNG

Associate attorney(s)

AUTHORIZATION TO CHARGE DEPOSIT ACCOUNTS FOR CITED REFERENCES

DEPOSIT ACCOUNT NO.	NO. OF COPIES
02-4740	2

Form PO-634 (10-61) U.S. DEPT. OF COMM. PATENT OFFICE

PARTS OF APPLICATION FILED SEPARATELY

PREPARED FOR ISSUE

(Assistant Examiner) (Docket Clerk)

EXAMINED AND PASSED FOR ISSUE

(Primary Examiner) (Division)

NOTICE OF ALLOWANCE MAILED

FINAL FEE

Date (Initial)

[THIS SPACE RESERVED FOR RETENTION LABEL]

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FEB 10 1964 U.S. PAT. OFF.

BURGESS, DINKLAGE & SPRUNG
Attorneys
233 BROADWAY
NEW YORK 7, N. Y.

343705

Date: Feb. 6, 1964

Hon. Commissioner of Patents
Washington 25, D. C.

ON ALL PAPERS PLEASE
FURNISH OUR FILE NO.
Metco 305.3

Dear Sir:

Re the application of Ferdinand J. Dittrich and Arthur P. Shepard
for FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

we enclose

(x) Specification

(x) Oath, Power of Attorney and Petition

(x) 1 Sheet(s) Drawings

(x) 38 Claim(s) in excess of 20

(x) $68.00 filing fee (covered by enclosed check)

( ) Assignment

( ) $3.00 recording fee (covered by enclosed check)

( ) Priority is hereby claimed on the basis of the following:

Country	Serial No.	Date

Respectfully,

BURGESS, DINKLAGE & SPRUNG

BY Arnold J. Sprung

1/2

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E 476

Metco 305.3
AS:as

343705

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

This invention relates to the flame spraying of exothermically reacting intermetallic compound forming composites and is a continuation-in-part of copending application, Serial No. 72,543 filed November 22, 1960; Serial No. 134,544 filed August 16, 1961; and Serial No. 237,786 filed October 26, 1962. The invention more particularly relates to the flame spraying of flame spray materials in the form of composites containing two or more components which will exothermically react with each other during the spraying, forming one or more intermetallic compounds, and to a novel group of such composites including powders and wires.

Flame spraying involves the feeding of a heat-fusible material into a heating zone, wherein the same is melted or at least heat-softened, and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone formed by a flame of some type, where it is melted or at least

heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by sintering together finely divided material, or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly produced from a flame caused by the combustion of a fuel,

such as acetylene, propane, natural gas, or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or, in the newer type of guns, by a plasma flame. The plasma flame may in itself constitute part of an electric arc, or, in accordance with a newer development, may be in the form of a "free plasma stream", i.e., a stream of plasma which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead and zinc.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets, and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic, or the like. While it is true that rods or wires formed from finely divided material bound together with a binder of plastic or the

like, as mentioned above, were known, the binder generally did not take part in the spraying or contribute to the coating, and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spray materials.

These and still further objects will become apparent from the following description read in conjunction with the drawing in which:

Fig. 1 diagrammatically shows a cross-section of a grain of novel powder in accordance with the invention;

Fig. 2 is a cross-section of a further embodiment of an aggregate grain of novel flame spray powder in accordance with the invention;

Fig. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray wire in accordance with the invention;

Fig. 4 shows a cross-section of a further embodiment of a novel flame spray wire in accordance with the invention; and

Fig. 5 shows a still further embodiment of a novel flame spray wire in accordance with the invention.

In accordance with the invention, the flame spraying is effected with the heat-fusible material in the form of a composite containing at least two components which will exothermically react with each other at the temperatures developed during the spraying, forming an intermetallic compound.

The term "composite" as used herein is intended to designate a structurally integral unit and does not include a mere mixture of components which may be physically separated without any destruction of the structure. Thus, in the case of powder, the term "composite" does not include a simple mixture of individual granules of the separate components, but requires that each of the individual granules contain the separate components which will exothermically react, forming intermetallic compounds. In the case of wire, the individual components must be incorporated in a single wire. In the composite, the components must be in intimate contact with each other.

In connection with powders, each grain may consist of an aggregate containing the two components which will exothermically react, forming the intermetallic compound, but preferably the individual grains of the powder are in the form of a clad composite consisting of a nucleus of one of the components and at least one coating layer of the other component. Alternatively, the composite may

consist of separate, concentric coating layers of the two components and a nucleus of still a third material.

In the case of wires, the composites may be in the form of a wire having a coating sheath of one material and a core of the other, alternate coating sheaths of the components and a core of a third material, a wire formed by twisting or rolling separate wire strands of the components, a wire consisting of a sheath of one component and a core containing the other component in powder or compacted form, a wire consisting of a sheath of one component and a core containing a compacted powder mixture of this same component material and one or more other components, a wire consisting of a plastic sheath and a core containing a compacted powder mixture of components, etc.

As the components, any two metallics which may be melted together to form an intermetallic compound in an exothermic reaction may be used. The components should release about 3000 calories per gram atom, and preferably at least 7500 calories per gram atom in the exothermic reaction forming the intermetallic compounds. The term "calories per gram atom" as used herein denotes the number of gram calories which the average atomic weight in grams of the intermetallic compound formed will generate in so being formed. While the components are preferably present in the stoichiometric proportions required for the formation of the intermetallic compound, it is, however, possible to also have an excess of

one or the other provided the relative amounts are sufficient to release the quantities of heat indicated above in the formation of the intermetallic compounds.

An extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat. Any of these component pairs may be utilized in accordance with the invention, it only being required that the same be capable of being initially formed into the composite suitable for spraying and that the intermetallic compounds formed therefrom liberate the required amount of heat in the intermetallic compounds-formation and are suitable as components of a sprayed coating. As a general rule, components which will form intermetallic compounds having a higher melting point will liberate sufficient heat to be useful in accordance with the invention. In certain instances, however, components which will form intermetallic compounds which do not have as high a melting point, will also liberate sufficient heat in the exothermic reaction and thus be useful. Preferred components are aluminum with at least one of Co, Cr, Mo, W, Ta, Nb, Ti, or most preferably Ni; or silicon with at least one of Ti, Nb, Cr, W, Co, Mo, Ni or Ta.

Fig. 1 shows a composite powder consisting of a nucleus of aluminum and a coating layer of nickel. Fig. 2 shows an aggregate of these components; and Figs. 3, 4, and 5 show various forms of wire containing these components, Fig. 3 showing a wire having an aluminum core with a nickel

sheath, Fig. 4 showing a wire made of alternate strands of nickel and aluminum wire, as for example 18 strands of 25 gauge (.019" diameter) nickel wire marked 1, and 19 strands of 25 gauge aluminum wire marked 2; and Fig. 5 shows a sheath of aluminum filled with granules of nickel and aluminum.

Where one of the component metals is available as a metal hydride, the same may be used in this form rather than as a metal per se. When flame sprayed the hydrogen gas evolved from the hydride produces a reducing atmosphere, which in turn suppresses oxidation of the intermetallic compounds during and immediately after their formation. Thus, for example, in place of titanium, titanium hydride may be used as one of the components.

Also for the purpose of reducing oxidation a metal hydride, such as titanium hydride, may be added in a minor amount to the other components. Thus, for example, 1 - 10% by weight, and preferably 1 - 5% by weight, based on the total of the hydride and other components, may be used.

In addition, the powder granules and the wire may contain other conventional flame spray components, or be sprayed in admixture or in conjunction therewith. Thus, for example, the coated powders may additionally contain other coating layers of other flame spray components or may contain a nucleus of another flame spray material with alternate coating layers of the components which will exothermically react, forming the intermetallic. In a similar manner, the aggregates or the wires may contain further

flame spray components, and in the case of powders, the same may additionally be admixed with any other desired flame spray powder.

The clad powders, in accordance with the invention, may be formed in any known or desired manner, and preferably by the known chemical plating processes, in which coating material is deposited on a seed or nucleus of another material, or in which multiple layers of various materials are built up on the seed material, or in which various materials are co-deposited in a single layer on the seed material.

A mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as by the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulfate on a seed powder catalyzed by the addition of anthraquinone. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor deposition, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal deposition of halides, hydrides, carbonyls, organo metals, or other volatile compounds, or by displacement gas plating and the like.

A preferred and greatly simplified mode of forming the clad powders in accordance with the invention is the depositing of one component as a coating in the form of a paint on the other component. Thus, one of the

components which is to form the coating or cladding, may be dispersed in finely divided form in a binder or lacquer so as, in effect, to form a paint in which this component corresponds to the pigment. The paint is then used to coat core particles of the other component and the binder or lacquer allowed to set or dry. The binder material is preferably a resin which does not depend on solvent evaporation in order to form a dried or set film, and which film will decompose or break down in the heat of the spraying process. The binder, for example, may be a phenolic varnish or any other known or conventional varnish, preferably containing a resin as the varnish solids. The component which is initially mixed with the binder or varnish should preferably be as finely divided as possible, as for example -325 mesh. The other component which constitutes the core should be approximately or only slightly below the particle size ultimately desired for the spray powder. The coating of the core component with the "paint" may be effected in any known or desired manner, and it is simply necessary to mix the two materials together and allow the binder to dry or set, which will result in a fairly free-flowing powder consisting of the core component coated with a cladding of the other component bound in the binder.

The aggregates may be formed by compacting or briquetting the various components into the individual granules, or into larger aggregates and then breaking these aggregates into the granules.

The wires may be formed in the known conventional

manner for forming wires with various components as, for example, by shrinking a sheath on a core, by forming the core with powder, by twisting the component wires, followed by rolling, drawing, swaging, or the like if desired.

In accordance with one mode of manufacture, one of the components may be formed into a tube or sheath and filled with a powder of the other component or a powder comprising a mixture of the two components, or containing additional components. The tube ends are then sealed and the wire reduced to the desired wire diameter by swaging, rolling or drawing. Preferably the powder or powder mixture is first compressed into cylindrical briquettes before being placed in the sheath or core. The sealing of the tube ends after loading with the powder or powder mixture can be effected, for instance, by insertion of a plug, for example of the metal of the sheath, by welding, twisting, crimping, or the like.

Powders in accordance with the invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a size between -60 mesh and +3 microns and preferably -140 mesh and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the composite powders may be sprayed

per se or in combination with other different composite powders, or in combination with other conventional flame spray powders or powder components.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder, which decomposes in the heating zone of the gun, or in certain cases the powders may be compacted and/or sintered together in the form of a rod or wire. The wires must have the conventional sizes and accuracy tolerances for flame spray wires, and thus for example may vary in size between 1/4" and 20 gauge, and are preferably of the following sizes: 3/16" $\pm$ .0005" $-$.0025", 1/8" $\pm$.0005" $-$.0025", 11 gauge $\pm$.0005" $-$.0025", and 15 gauge +.001", with a smooth, clean finish free from surface marks, blemishes, or defects. The wires are sprayed in the conventional manner, using conventional wire-type flame spray guns.

In combining, in the exothermic reaction, forming the intermetallic compound, the components generate heat in situ in the actual material which is to form at least a part of the coating. This is to be distinguished from flame-spray processes and materials in which heat is generated by a reaction, such as an oxidation reaction, in which a foreign and non-metallic element is introduced and in which undesirable components may be produced. Aside from greatly contributing to the thermal efficiency of the process, the heat generated in situ in the formation of the intermetallic

compound produces novel results, in many instances forming a denser, more adhering coating, having characteristics of at least a partially fused coating. In many instances the coating has self-bonding characteristics, so that special surface preparation, other than a good cleaning, is not required. The spraying in all other respects is effected in the conventional, well-known manner, using conventional flame spray equipment, and the conventional surface preparation may be utilized, if desired. The composites in accordance with the invention may be sprayed in conjunction with, or in addition to, other flame spray materials conventionally used in the art, may be sprayed in combination or conjunction with the others.

The use of the composites as, for example, the nickel-aluminum composites, will generally improve the bond of the total sprayed material, and thus of the other component or components to the substrate, sometimes making the mixture self-bonding. The particle bond will be improved and the coating will be denser, so that its porosity may be decreased. In general, as little as 10% by weight of the composites in accordance with the invention will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame spray materials, such as conventional flame spray metals, alloys or ceramics. There is, of course, no upper limit on the amount, as the composite may be sprayed per se, but generally at least about 20% by weight of the other component is required if this component is to have a pronounced effect on the characteristics

of the coating.

The following examples are given by way of illustration and not limitation:

EXAMPLE I

(a) An aluminum powder having a particle size between -140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate, using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 300 and 350° F. in a mechanically agitated autoclave using solutions containing 40-50 grams per liter of nickel and 10-400 grams per liter of $(NH_4)_2SO_4$ and 20-30 grams per liter of NH_3. About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i.g. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder is formed containing about 16 to 18% by weight

aluminum and 84 to 82% by weight of nickel, and a size of -100 to +270 mesh.

The powder thus formed is flame-sprayed on mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 9 inches from the plate, using a powder-type flame-spray gun as described in U.S. Patent 2,961,335, issued November 22, 1960 and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermospray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel at a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu.ft./hr. and oxygen as the oxidizing gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu.ft./hr.

The nickel coating and the aluminum base coabine in the heat of the flame with a strong exothermic action, forming a mixture of nickel aluminum intermetallic compounds which deposit on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002" - .004" thickness is built up in this manner. The coating may be used as a base material for spraying further layers of different metals or the like, and serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .010" - .020", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020" - .040" or thicker as a wear-resistant - oxidation-resistant surface.

Due to its self-bonding characteristics the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the powder has excellent oxidation-resistant characteristics even at high temperatures and in oxidizing atmospheres, and will for example prevent the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature , wear-resistant coatings.

When the example is repeated on a molybdenum rod of 3/18" diameter, with a coating between .010" - .012" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, in an electric furnace and cooled to room temperature

with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10 - 45% by weight of aluminum and 55 - 90% by weight of nickel.

(b) Example 1(a) is repeated, using, however, cobalt in place of the nickel. Comparable results are obtained.

(c) Example 1(a) is repeated, using titanium hydride (TiH_2) powder in place of the aluminum and in an amount of 25 - 85 weight %, and preferably 60 - 85 weight % of the total. The coating formed upon spraying is hard and dense, and when sprayed on a smooth, pressed and sintered Al_2O_3 substrate, an excellent bond is formed. The spraying may be effected with an oxygen-hydrogen or oxygen-acetylene flame.

EXAMPLE 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough-ground or light-grit-blasted; and titanium, rough-ground or light-grit-blasted.

In each case when a further material, such as steel, alumina or the like, was sprayed over the coating in the conventional and well known manner, the same was bonded with a tenacious bond, though if this material had been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

EXAMPLE 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface-cleaned by smooth grinding. Spraying is effected at a distance of about 9" from the plate at a rate of about 4 to 8 lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17 - 25 cu.ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29 - 35 cu.ft./hr.

A self-bonding cermet coating is formed which showed excellent thermal shock-resistance, hardness, abrasion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an

increased amount of the intermetallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic, the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

EXAMPLE 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium zirconate, spinel, ceric oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium silicide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

EXAMPLE 5

A nucleus of silicon powder is coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 75 - 85% nickel based on the silicon-nickel total. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying silicon combines

with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating.

EXAMPLE 6

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 50% nickel based on the titanium-nickel total.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the nickel and titanium combine exothermically in the flame to form a corrosion-resistant coating comprising a nickel-titanium intermetallic compound.

EXAMPLE 7

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 50 to 80% copper based on the tellurium-copper total.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved

upon the combination of the copper and tellurium, increasing the thermal economy of the process.

EXAMPLE 8

The nickel-clad flame spray powder of Example 1 is mixed with about 20% by weight of low pressure polyethylene powder and molded at a temperature of about 212° F. into the form of a rod of 1/8" diameter. The rod is sprayed, using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E Gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu.ft./hr; with air as a blast gas at a pressure of 40 p.s.i. and a flow rate of 25 cu.ft./min. The end coating produced is similar to the coating produced in Example 1.

EXAMPLE 9

A wire is formed by encasing a core of nickel in a tube of aluminum and drawing to a size of .125" in diameter plus or minus .002. The wire contains 82 to 84% by weight of nickel based on the aluminum-nickel total.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E Gun. Spraying is effected with acetylene

at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as the oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu.ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu.ft./min. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55 - 90% by weight of nickel in the wire.

EXAMPLE 10

A composite wire is formed by winding individual wires of nickel and aluminum to form a stranded wire with a diameter of .125" plus or minus .002". The wire contains 55 to 90% by weight of nickel based on the total Al-Ni. The wire is sprayed in the manner described in Example 9, with identical conditions and coating resulting.

EXAMPLE 11

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

EXAMPLE 12

A molybdenum powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using a mixture of argon and hydrogen gas as the plasma gas, with argon at a pressure of 100 p.s.i. and a flow rate of 110 cu.ft./hr., and hydrogen at 50 p.s.i. and a flow rate of 25 cu.ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of

15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 13

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation

at elevated temperatures and will protect the base material from oxidation.

EXAMPLE 14

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu.ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits

excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 15

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 45% zirconium and 60% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

EXAMPLE 16

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light

grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu.ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The titanium base and silicon coating combine exothermically in the heat of the flame, forming a titanium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 17

A dysprosium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a

base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 18

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine exothermically in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 19

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is

mad consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the chromium base combine in the heat of the flame with a strong exothermic action, forming a chromium aluminum intermetallic compound which deposits on the base as a dense, high quality coating of very high melting point and excellent oxidation-resistance.

EXAMPLE 20

Example 19 is repeated except that the composite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

EXAMPLE 21

The nickel-clad aluminum composite powder of Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of -140 mesh +10 microns, and preferably -140 +325 mesh in proportions of:

a) 80 weight percent tungsten carbide to 20 weight percent of the composite,

b) 20 weight percent of the carbide to 80 weight percent of the composite, and

c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface-cleaned by grinding or very light sand-blast cleaning. The spraying is effected at about 8 - 9 inches from the plate, using a powder-type flame-spray gun as described in U.S. Patent 2,961,335 issued November 22, 1960, and sold by Metco Inc. of Westbury, Long Island, New York, under the tradename of "Thermo-Spray" powder gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 p.s.i. and a flow rate of 20 to 30 cu.ft./hr. and oxygen as the oxidizing gas at a pressure of 14 p.s.i. and a flow rate of 30 to 40 cu.ft./hr.

The nickel-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on impact with the substrate, becomes the matrix which securely binds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by proper grinding procedure, the resultant coating is of a highly wear-resistant coating material, applicable to virtually any base material and not subject to the limitations of the previously used self-fluxing alloy matrix materials which must be fused at approximately 1900° F.

EXAMPLE 22

Example 21 is repeated except that in place of the grade of tungsten carbide cobalt powder grains used, cobalt-bonded tungsten carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 21. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resistant coating or used as deposited where the coated article is to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

EXAMPLE 23

Example 22 is repeated except that in place of the tungsten carbide grains described, cobalt-bonded tungsten carbide particles of sharp, angular shape were used which were first coated with nickel in the manner described in Example 1, so as to produce nickel-clad particles having a size between 100 and 325 mesh and containing from 20 - 50% nickel based on the tungsten carbide-nickel total.

EXAMPLE 24

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, is a highly wear-resistant, hard coating.

EXAMPLE 25

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, presents a highly wear-resistant, hard surface.

EXAMPLE 26

Example 21 is repeated except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium carbide, chromium carbide and mixtures of the various carbides are used.

EXAMPLE 27

The nickel-clad aluminum core composite from Example 21 is mixed with aluminum powder in the mesh size range -100 +325 mesh, and preferably in the -170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 21. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat-treating in the temperature range 1250° F. to 1500° F. in reducing atmosphere, dry hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogenous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt-water corrosion.

EXAMPLE 28

The nickel-clad aluminum composite powder of Example 21 is mixed with Monel powder of a size between -100 mesh and +10 microns, and preferably between -140 and +325 mesh in the proportions 35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, considerably increase the particle to particle bonds within the coating and decrease the permeability of the coating.

EXAMPLE 29

Example 28 is repeated except that nickel and stainless steel powders are substituted for the Monel.

EXAMPLE 30

Example 28 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished, by grinding or other means, shows high resistance to abrasion, wear, and galling by other metals, and is an excellent bearing surface.

EXAMPLE 31

Finely divided aluminum powder (-325 mesh) was blended with a phenolic varnish having approximately 50% solid contents so as to form a mixture having the consistency of a heavy syrup and containing 60% by weight of the metallic aluminum.

100 grams of this varnish aluminum powder mixture was added to 240 grams of nickel powder having a size between -200 and +325 mesh, and the two were thoroughly mixed, with the mixing continued until the varnish dried, leaving a fairly free-flowing powder in which all of the nickel core particles were clad with a dry film, which consisted of aluminum particles bonded to each other and to the core material by the phenolic binder. The powder is then warmed to 250° F. to insure complete drying. There were some minor agglomerates which were screened out and hand-milled to reduce the same to a -100 mesh powder. The end powder consisted of approximately 15 weight % aluminum and 85 weight % nickel due to the loss of some aluminum during the milling. The powder is sprayed in the manner described in Example 1 producing a similar coating having, however, more than twice the tensile strength of the coating produced in Example 1.

EXAMPLE 32

(a) A mixture of 6 weight % aluminum and 94 weight % nickel powder are thoroughly blended and pressed together in the form of cylindrical briquettes which are loaded into an aluminum tube of .375" outside diameter, after which the tube ends are welded closed. The 3/8" diameter feed stock is then swaged to 1/4" diameter, then to a 3/16" diameter and then to a 1/8" finished wire diameter. The wire is then annealed and coiled. The wire is then sprayed, using the conventional wire type flame spray gun sold by Metco Inc. as the Metco Type 4-E Gun. Spraying is effected, using acetylene at a pressure of about 15 lbs. p.s.i. and a flow rate of 37 cu.ft./hr. and oxygen as the oxidizing gas at a pressure of 38 lbs. p.s.i. and flow rate of 75 cu.ft./hr. Air is used as a blast gas at a pressure of 55 lbs. p.s.i. and flow rate of 30 cu.ft./min. The wire is sprayed at a rate of 5 ft. per minute. The spray material is deposited on a surface of ground and machine-finished, cold rolled steel with a tensile bond strength of 3840 lbs. p.s.i. The sprayed coating is hard and dense; it is wear- and oxidation-resistant and it also could serve as a base for further spraying.

(b) Example 32(a) is repeated except that chromium is used in place of the nickel powder

in amounts of from 24 - 95 weight %, based on the total of the aluminum and chromium. Spraying results in a high quality coating which has self-bonding properties and is resistant to oxidation at high temperatures.

(c) Example 32(a) is repeated, using columbium powder in place of the nickel powder in amounts of from 40 - 90 and preferably 50 - 55 weight %, based on the total of the columbium and aluminum. The sprayed coating formed is a high quality coating which is resistant to oxidation at high temperatures and may be used to protect tantalum and molybdenum bases from oxidation.

(d) Example 32(a) is repeated, using tantalum powder in place of the nickel powder in amounts of 40 - 90 weight % and preferably 65 - 75 weight % of tantalum, based on the total of tantalum and aluminum. The sprayed coating is a dense, high quality coating which is self-bonding and is resistant to oxidation at high temperatures.

(e) Example 32(a) is repeated, using boron powder in place of the nickel powder in amounts of 40 - 90 weight %, based on the total of boron and aluminum. The resulting sprayed coating is self-bonding and is resistant to oxidation at high temperatures.

(f) Example 32(c) is repeated except that the powder additionally contains 0.5 to 5 weight %

of boron, and/or 0.5 to 5 weight % of silicon, based on the total of the components. The coating formed is similar to that obtained in Example 32(c) except that on heating to high temperature in air, a very thin, dense, adherent, protective oxide film forms on the surface of the intermetallic compound formed, which is resistant to spalling due to thermal shock, and which is believed self-healing.

(g) Example 32(a) is repeated except that tungsten carbide containing 12% binder and having a particle size below -140 mesh is added in amount of 5 - 70 weight %, based on the total of the components. The resulting coating is a dense, extremely wear-resistant coating, which has self-bonding properties. This example may be further repeated, using in place of the tungsten carbide specified, crystalline tungsten carbide, aluminum oxide, diamonds or any other abrasive material.

(h) Example 32(a) is repeated. However, 1 - 10% by weight and preferably 1 - 5% by weight of titanium hydride of a size below -100 mesh and preferably below -325 mesh, based on the total of the components, is added to the core material. The results are the same as indicated in Example 32(a) except that the coating formed is of improved physical strength, containing considerably less oxide inclusions. In place of the titanium hydride other metal hydrides

(i) Example 32(a) is repeated except that the nickel powder is replaced with a nichrome powder consisting of a chrome alloy containing 80% nickel and 20% chromium. When sprayed the wire gives a dense, self-bonding coating which is extremely oxidation-resistant.

(j) Example 32(a) is repeated except that the nickel powder is replaced with a powder mixture consisting of 80% by weight nickel and 20% by weight chrome. When sprayed the wire gives a dense, self-bonding coating which is highly oxidation-resistant.

EXAMPLE 33

Table I below gives examples of further component pairs which may be used to form the powders and/or wires in accordance with the invention.

Each of the component pairs as listed in Table I below may be formed into a composite powder or wire as described above, and when flame-sprayed will exothermically react, forming an intermetallic compound and high grade coating. Thus, the component pairs may be formed into clad powders as described in Example 31 and sprayed as described therein, or formed into a composite wire as described in Example 32 and sprayed as described therein.

Table I

Ag Ce	As In	Bi Mg	In Te	Pb Pu
Al As	As Mg	Bi Na	In Ru	Pb Se
Al Au	As Zn	Bi Se	K Sb	Pb Tl
Al B	B Y	Bi Te	K Se	Pd U
Al Ba	B Ca	Bi Th	K Sn	Pr Sn
Al Ca	B Cr	Bi Pb	K Te	Pr Tl
Al Ce	B Hf	Ca Sn	La Pb	Sb Zr
Al Co	B Nb	Ca Tl	La Sb	Se Sn
Al Cr	B Ta	Cd Li	La Sn	Se Th
Al La	B Th	Cd Na	La Te	Se Tl
Al Li	B Ti	Ce In	La Zn	Sn Te
Al Mo	B V	Ce Mg	Li Pb	Si Ti
Al Nb	B W	Ce Pb	Li Sb	Si U
Al Ni	B Zr	Ce Si	Li Sn	Si V
Al Pr	Ba Bi	Ce Sn	Li Tl	Si Zr
Al Ti	Ba Pb	Ce Tl	Li Zn	Sn Te
Al Zr	Ba Sb	Ce Zn	Mg Sb	Sn U
Al Sb	Be Co	Ga Na	Mg Sn	Sn Zr
Al Se	Be Cr	Ga Pr	Na Pb	Te Zn
Al Ta	Be Ni	Ga Sb	Na Sb	Mo Be
Al Te	Be Np	Ga Te	Na Se	Nb Be
Al U	Be Pu	Ga U	Na Sn	Ta Be
Al V	Be U	Ge Mg	Na Te	V Be
Al W	Be Zr	Ge Nb	Na Tl	Ti Be
As Cd	Bi Ca	Ge Zr	Nb Si	Cr Si
As Ga	Bi Ce	H Y	Ni Th	Cr Ti
	Bi K	Li In	Pb Pr	Cr Zr
	Bi Li			

TABLE I(continued)

Fe Si

Mg Te

Ni Te

Si Th'

Si W

Co Si

Mo Si

Ni Si

Si Ta

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention therefore is only intended to be limited by the appended claims or their equivalents, wherein we have endeavored to claim all inherent novelty.

We claim:

1. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in such condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite comprising at least two components which exothermically react with each other at the temperature developed in the heating zone, forming an intermetallic compound.

2. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

3. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

4. Improvement according to claim 1 in which one of said components is aluminum and the other nickel.

5. Improvement according to claim 4, in which said aluminum is present in amount of about 10 to 45% by weight, based on the total of nickel and aluminum.

6. Improvement according to claim 1 in which said components are component pairs selected from the group listed in Table I above.

7. Improvement according to claim 1 in which said composite contains at least one additional flame spray material.

8. Improvement according to claim 1 in which said composite is sprayed in conjunction with at least one further flame spray material.

9. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of individual clad powder particles comprising a nucleus and a coating layer which will exothermically react with the nucleus at the temperature developed in the heating zone, forming an intermetallic compound.

10. Improvement according to claim 9 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

11. Improvement according to claim 9 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

12. Improvement according to claim 9 in which said nucleus is aluminum and said coating layer nickel.

13. Improvement according to claim 12 in which said aluminum is present in amount of about 10 - 45%, based on the total of nickel and aluminum.

14. Improvement according to claim 9 in which the nucleus and coating layers are selected from the members of the group consisting of the pairs listed in Table I.

15. Improvement according to claim 9 in which said coating layer consists of fine particles bound to said nucleus by a binder.

16. Improvement according to claim 9 in which said clad powder particles are in admixture with another flame spray powder.

17. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite wire comprising at least two components which exothermically react with each other at the temperatures developed in the heating zone, forming an intermetallic compound.

18. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

19. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

20. Improvement according to claim 17 in which one of said components is aluminum and the other nickel.

21. Improvement according to claim 20 in which said aluminum is present in amount of about 10 - 45% by weight, based on the total of nickel and aluminum.

22. Improvement according to claim 17 in which said components are component pairs selected from the group listed in Table I above.

23. Improvement according to claim 17 in which said wire is in the form of a sheath of one component containing a powder of the other component.

24. Improvement according to claim 23 in which said sheath is an aluminum sheath and in which said core is a compacted mixture of aluminum and nickel powder.

25. Improvement according to claim 17 in which said wire is a multi-strand wire with individual strands of said components.

26. A flame spray material suitable for use in the process of claim 1, comprising a composite containing at least two components which exothermically react with each other when melted, forming an intermetallic compound.

27. A flame spray material suitable for use in the process of claim 1, comprising a composite containing at least two components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 3,000 gram calories per gram.atom.

28. A flame spray material suitable for use in the process of claim 1, comprising a composite containing at least two components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 7,500 gram calories per gram.atom.

29. A flame spray material suitable for use in the process of claim 1, comprising a composite containing aluminum and nickel.

30. Composite according to claim 29 in which said aluminum is present in amount of about 10 - 45%, based on the total of nickel and aluminum.

31. Composite according to claim 26 in which said components are component pairs selected from the group listed in Table I above.

32. A flame spray powder in the form of individual clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound.

33. A flame spray powder in the form of individual clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 3,000 gram calories per gram atom.

34. A flame spray powder in the form of individual clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom.

35. A flame spray powder according to claim 32 in which said components are component pairs selected from the group listed in Table I above.

36. A flame spray powder according to claim 32 in which said coating layer is in the form of a finely divided powder bound to the nucleus by a binder.

37. A flame spray powder in the form of individual clad particles comprising a nucleus of aluminum and a coating layer of nickel.

38. Powder according to claim 37 in which said aluminum is present in amounts of about 10 - 45%, based on the total of nickel and aluminum.

39. A flame spray powder in the form of individual clad particles comprising a nucleus of nickel and a coating layer of finely divided aluminum particles bound to the nucleus with a binder.

40. A flame spray wire suitable for use in the process of claim 1, comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound.

41. A flame spray wire suitable for use in the process of claim 1, comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom.

42. A flame spray wire suitable for use in the process of claim 1 comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, one of said components being aluminum and the other nickel.

43. A flame spray wire suitable for use in the process of claim 1 comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of 7,500 gram calories per gram atom, said components being component pairs selected from the group listed in Table I above.

44. A flame spray wire suitable for use in the process of claim 1 comprising a sheath of a first component and a powder core of at least one second component, said first and second components being capable of exothermically reacting with each other when melted together, with the release of at least 7,500 gram calories per gram atom.

45. A flame spray wire according to claim 44 in which said sheath is aluminum and said core a mixture of aluminum and nickel powder.

46. A flame spray wire suitable for use in the process of claim 1, comprising individual strands of two separate components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom.

47. A process for producing flame spray powder ~~according to claim 32~~, which comprises applying a coating of a finely divided powder in a binder to a nucleus powder and drying the binder, said first mentioned powder and said nucleus powder comprising materials which will exothermically react together, forming an intermetallic compound.

48. Process according to claim 47 in which said nucleus is nickel powder and said finely divided powder is aluminum powder.

49. Process according to claim 48 in which the aluminum powder dispersed in a phenolic varnish is admixed with the nickel powder and the varnish dried.

50. Improvement according to claim 1 in which the heat-fusible material additionally contains a metal hydride.

51. Process according to claim 50 in which one of said components is at least partially in the form of a hydride.

52. Flame spray material according to claim 26 additionally containing a metal hydride.

53. Flame spray material according to claim 26 in which one of the said components is at least partially in the form of a hydride.

54. Flame spray material according to claim 26 additionally containing a member selected from the group consisting of boron, silicon and mixtures thereof.

55. A flame spray material suitable for use in the process of claim 1 comprising a composite containing at least two components which exothermically react with each other when melted, said components being component pairs selected from the group consisting of Al Co, Al Cr, Al Mo, Al W, Al Ta, Al Nb, Al Ti, Al Ni, Si Nb, Si Cr, Si W, Si Co, Si Mo, Si Ni, and Si Ta.

56. A flame spray material according to claim 55 in the form of a powder.

57. A flame spray material according to claim 55 in which one of the components is in the form of a coating on the other component.

58. A flame spray material according to claim 55 in the form of a wire.

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OATH, POWER OF ATTORNEY and PETITION

Being duly sworn, we, Ferdinand J. Dittrich and Arthur P. Shepard, residing at 2457 New Place, Bellmore, Long Island, New York, and 29-01 - 159th Street, Flushing, Long Island, New York, respectively, depose and says that we are citizens of the United States; that we have read the foregoing specification and claims and we verily believe that we are the original, first and joint inventors of the invention or discovery of FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES described therein; that this application discloses and claims subject matter disclosed in our pending applications, U. S. Serial No. 72,543 filed November 22, 1960; U. S. Serial No. 134,544 filed August 16, 1961, and U. S. Serial No. 237,786 filed October 26, 1962; that as to the subject matter of this application which is common to said application we do not know and do not believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than one year prior to said application, or in public use or on sale in the United States for more than one year prior to said application; that said common subject matter has not been patented before the date of said application in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months prior to said application; that as to the subject matter of this application which is not common to said application we do not know and do not

believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than one year prior to this application, or in public use or on sale in the United States for more than one year prior to this application, and that said subject matter has not been patented in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months prior to this application; and that no application for patent on said invention has been filed by us or our representatives or assigns in any country foreign to the United States, except as follows: Argentina, filed September 14, 1961; Belgium, filed November 21, 1961; France, filed November 17, 1961; Spain, filed September 29, 1961; Australia, filed September 19, 1961; Canada, filed November 8, 1961; Germany, filed October 24, 1961; Great Britain, filed September 14, 1961; Holland, filed October 13, 1961; India, filed August 22, 1961; Italy, filed September 27, 1961; Japan, filed November 22, 1961; Mexico, filed October 20, 1961; Sweden, filed October 27, 1961; Switzerland, filed October 31, 1961; India, filed May 21, 1963.

And we hereby appoint BURGESS, DINKLAGE & SPRUNG (Registration No. 15,379) a firm composed of Ralph D. Dinklage and Arnold Sprung, of 233 Broadway, New York 7, New York, our attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith.

WHEREFORE we pray that Letters Patent be granted to us for the invention or discovery described and claimed in the foregoing specification and claims, and we hereby subscribe our names to the foregoing specification and claims, oath, power of attorney and this petition, this 31st day of January, 1964.

Inventor: Ferdinand J. Dittrich
2457 New Place, Bellmore, Long Island, New York

Inventor: Arthur P Shepard
29-01 - 159th Street, Flushing, Long Island, New York

STATE OF NEW YORK)
) ss:
COUNTY OF NASSAU)

Before me personally appeared FERDINAND J. DITTRICH and ARTHUR P. SHEPARD, to me known to be the persons described in the above application for patent, who signed the foregoing instrument in my presence, and made oath before me to the allegations set forth therein as being under oath, on the day and year aforesaid.

John J Donovan

JOHN J. DONOVAN
Notary Public, State of New York
No. [illegible]
Qualified in Nassau County
Commission Expires March 30, 1964

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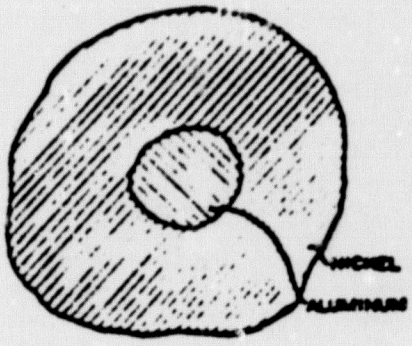

Fig. 1

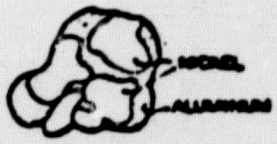

Fig. 2

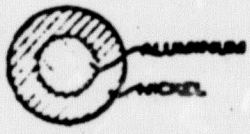

Fig. 3

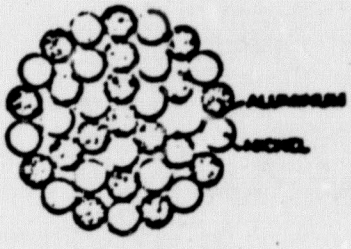

Fig. 4

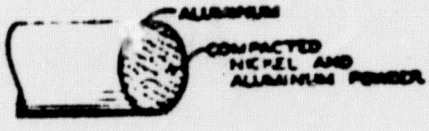

Fig. 5

INVENTORS
FERDINAND J. DITTRICH
ARTHUR P. SHEPARD

BY Burgess Dunlap & Sprung
ATTORNEYS

ME 3053

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Form No. 3

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

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In Reply Please Refer To

Burgess, Dinklage and Sprung
233 Broadway
New York 7, New York

Applicant: Ferdinand J. Dittrich et al.
Ser. No. 343,705
Filed Feb. 10, 1964
For FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

MAILED
NOV 23 1964
GROUP 160

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

SHORTENED TIME FOR REPLY

This application has been examined.

Patents cited to show classification:

I.	1,971,804	4/34	Alexander	117-46
	2,208,869	7/42	Wasserman	117-46
II.	1,379,063	5/21	Van Allen	29-191
	2,933,415	4/61	Homer	29-191
III.	1,916,989	7/33	Rader	29-191.6
	2,055,948	9/36	Selquist	29-191.6
IV.	2,303,504	12/42	Ryan	117-100
	2,853,403	9/58	Mackiw	117-100

This application is found to contain claims drawn to four separate and distinct inventions. Restriction as indicated below is required under Rule 142.

I. Claims 1 to 25, 50 and 51 drawn to process of flame spraying and a flame sprayed article, classified with the Alexander and Wasserman patents.

II. Claims 26 to 39 and 52 to 57 drawn to composite metal stock particles, classified with the Van Allen and Homer patents.

III. Claims 40 to 46 and 58 drawn to composite metal wire, classified with the Rader and Selquist patents.

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IV. Claims 47 to 49 drawn to a process of applying a coating to a particulate powder, classfied with the Ryan and Mackiw patents.

The inventions are distinct from the other because the composite powder of Group II and the composite wire of Group III have differenct utility other than in the flame spraying process defined in the claims of Group I. For example, the composite metal powder of the claims in Group II could be used in the fabrication of metal parts from the compressed compacted powder, as shown by the Homer et al. patent, or in a sintering process. The metal wire of Group III could be used as anchoring and sealing wire as illustrated by the Rader patent, or as an electrical conductor illustrated by the Selquist patent. Also for the above reasons the classification of Group II drawn to a powder and Group III drawn to a wire have acquired separate status in the art.

The process of Group IV is distinct from Groups I to III as illustrated by the Mackiw drawn to a method of making a composite metal particle, and the Ryan patent illustrating the treatment of metal powders.

The claims as grouped thus define separate-through-related- inventions, not mutually dependent upon each other, capable of supporting separate patents. M.P.E.P. 806.03.

Asshown by the exemplary patents cited, the several alleged inventions have attained separate status

in the art and are separately classified so as to require divergent searches. M.P.E.P. 808.

Since (a) the claims, as grouped above, define separate inventions capable of supporting separate patents and (b) reason exists for insisting upon restriction, the restriction requirement is deemed proper.

Attention is directed to the provisions of Rule 143 and M.P.E.P. 818 through 818.03(c) for factors pertinent to an election and complete response.

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE TWO MONTHS FROM THE DATE OF THIS LETTER.

Attention is directed to the Commissioner's address published in the 803 O.G. 893.

Examiner

AG
A.Golian:meb
WO 7-2525

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Metco 305.3
DEC 1- 1964

IN THE UNITED STATES PATENT OFFICE

GROUP 160

Applicants: Ferdinand J. Dittrich and Arthur P. Shepard

Serial No.: 343,705

RECEIVED
NOV 25 1964
Group 110
GROUP 160

Filed : February 10, 1964

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

November 20, 1964

Hon. Commissioner of Patents
Washington 25, D.C.

Sir:

BURGESS, DINKLAGE & SPRUNG, attorneys of record in the above entitled application, announce their change of address as of April 30, 1964 to 605 Third Avenue, New York City, N.Y. 10016, and respectfully request that all future correspondence and actions be addressed to them at that address.

Very truly yours,

BURGESS, DINKLAGE & SPRUNG

By _____
Attorneys for Applicants

JAN 25 1965

E 535

IN THE UNITED STATES PATENT OFFICE

RECEIVED
JAN 27 1965
GROUP 1

APPLICATION OF: FERDINAND J. DITTRICH, ET AL.

SERIAL NO.: 343,705

FILED: FEBRUARY 10, 1964

FOR: FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITE

GROUP: 160

Washington, D. C.

January 25, 1964

Hon. Commissioner of Patents
Washington, D. C. 20231

Sir:

AMENDMENT

In reply to the Official Action dated November 23, 1964, requiring restriction, the applicants hereby provisionally elect Group I comprising claims 1 to 25, 50 and 51, which are drawn to the process of flame spraying and to flame sprayed articles.

The applicants respectfully request reconsideration of the requirement for restriction on the ground that the claims do not define independent and distinct inventions.

The applicants reserve the right to file one or more divisional applications directed to the non-elected claims should this requirement be made final.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

Attorneys for Applicants

by Plumley, Tyner & Sandt

Washington, D. C.
Representative

JAN 28 1965 U.S. PATENT OFFICE

Metc. 305.3
AS/k

Group 160

RECEIVED
FEB 1- 1965
GROUP 160

E 536

IN THE UNITED STATES PATENT OFFICE

Applicants: Ferdinand J. Dittrich et al

Serial No.: 343 705

Group 160

Filed : February 10, 1964

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES.

January 27, 1965

Hon. Commissioner of Patents
Washington, D. C.

Sir:

The following is supplemental to our amendment dated January 25, 1965.

The Office Action of November 23, 1964 was responded to by a request for reconsideration of the requirement for restriction and a provisional election of Group I comprising claims 1 to 25, 50 and 51. Applicants hereby request permission to shift the provisional election to Group IV comprising claims 47 to 49. It is believed that this shift should be permitted as it is assumed that the Examiner has not yet acted in reliance on the previous provisional election made.

The non-elected claims are retained for divisional purposes should the requirement be made final.

Respectfully submitted,
BURNESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

Paper No. 7

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 537

In Reply Please Refer To:

Burgess, Dinklage and Sprung
605 Third Avenue
New York, N. Y. 10016

Applicant: Ferdinand J. Dittrich et al.
Ser. No. 343,705
Filed Feb. 10, 1964
For: EXOTHERMICALLY REACTED INTERMETALLIC CO[illegible] FORMING COMPOSITE

APR 26 1965

GROUP 200

SHORTENED TIME FOR REPLY

Card Reference Charge Data (if applicable)	
Deposit Account No.	No. of Copies
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Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

This is in response to the letters filed January 25, and January 28, 1965.

References applied:

2,370,242	2/45	Hansel et al.	117-100N
2,853,403	9/58	Mackiw et al.	117-100K
2,967,787	1/61	Hoyt	117-100 I
3,102,044	8/63 (9-12-60)	Joseph	117-22

Art cited of interest:

2,273,832	8/40	Carney	117-100M
2,775,933	1/57	Wade	117-100K
2,976,166	3/61	White tetal.	117-46 FS
3,025,182	4/62 (3-3-58)	Schrewelius	117-105
3,050,409	8/62 (11-30-59)	Bayer	117-22

Claims 47 to 49 have been elected by applicant due to the requirement for restriction, the election made without traverse in Paper No. 6.

The specification is objected to since the Table on page 40 shows the combinations of sodium with other metals and the combination of hydrogen with vanadium. The specification is considered incomplete since it is felt that special precautions would be necessary due to the reactiveness of sodium. Yet the specification is silent on any procedures of this nature. Also it is not seen how vanadium could be applied to hydrogen through a binder.

Claims 47 to 49 are rejected on insufficient disclosure for the reasons set forth in the preceding paragraph.

Claims 47 to 49 are rejected as failing to properly define the invention as required under 35 U.S.C. 112. The phrase "according to claim 32" renders the claim indefinite and should be removed.

Claims 47 and 48 are rejected as unpatentable over Hensel et al. per se or further in view of Joseph or Mackiw et al. under 35 U.S.C. 103. Hensel et al. teach the process of coating a powder with an adhesive and coating this substrate with another metal. Also the second metal may be applied in the form of a paste. Since most metals will react exothermally to form intermetallic compounds, the metals of Hensel et al. are seen to be equivalent to applicant's metals. The Joseph and Mackiw et al. references have been applied merely to

show the wide variety of metal particles which have been coated with other metals. Note for example, the Joseph reference on column 2, lines 7 to 18 and the first complete paragraph of column 3.

Claim 49 is rejected on the references and the reasons applied to claim 47 further in view of Hoyt. This latter reference shows that phenols are known adhesives for particulate material. Only the expected results are obtained in the choice of a particular type of adhesive.

The Carney, Wade, White et al., Schrewelius and Bayer references, cited of interest, teach the employment of powders.

Summary:

Claims non-elected without traverse in Paper No. 6: 1 to 46 and 50 to 58.

Claims rejected: 47 to 49.

Claims allowed: none.

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE FOUR MONTHS FROM THE DATE HEREOF.

Richard D. Lovus
Examiner

A.G.:meb
WO 7-2367

64

APR 28 1965 U.S. PAT. OFFICE

E 540 60-18

AC/ip

#8

IN THE UNITED STATES PATENT OFFICE

RECEIVED MAY 3 1965 GROUP 160

Applicant(s) : Ferdinand J. Dittrich & Arthur P. Sh

Serial No. : 343,705

Filed : February 10, 1964

Group 160

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES.

April 27, 1965

Hon. Commissioner of Patents
Washington, D.C. 20231

Sir:

Account No. 02-4740

You are hereby authorized to furnish us with the following references cited in future Office Actions in the above application. Charge the cost thereof to the above account.

~~1 copy~~)
2 copies) U. S. patents

~~1 copy~~)
2 copies) Foreign patents

~~1 copy~~)
2 copies) Literature references

Respectfully,

BURGESS, DINKLAGE & SPRUNG

BY _____
Attorneys for Applicant(s)

E 541

#9

RECEIVED Metco 305. AS/k

MAY 21 1965

MAIL ROOM MAY 19 1965 U.S. PATENT OFFICE

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 343 705 Group 160

Filed : February 10, 1964

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

May 18, 1965

Hon. Commissioner of Patents
Washington, D. C.

Sir:

The following is in response to the Office Action dated April 26, 1965.

Kindly enter the following amendment:

In the specification, cancel the first sentence and substitute the following --This is a continuation-in-part of copending application Serial No. 72 543, filed November 22, 1960; Serial No. 134 544, Filed August 16, 1961; and Serial No. 237 786 filed October 26, 1962. The invention relates to the flame spraying of exothermically reacting intermetallic compound forming composites.--

Page 40, Table 1, third column, next to the last line, cancel " H V ".

Claim 47, line 2 cancel "according to claim 32" and substitute --in the form of individually clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and exothermically reacting therewith when melted together forming an intermetallic compound --

66

Kindly add the following claims:

59. Process according to claim 47 in which said first mentioned powder and said nucleus powder comprise materials which will exothermically react with each other when melted together forming an intermetallic compound with the release of at least 3000 gram calories per gram atom.

60. Process according to claim 59 in which said first mentioned powder and said nucleus powder comprise materials which will form an intermetallic compound having a nigher melting point than the components.

61. Process according to claim 47 in which said first mentioned powder and said nucleus powder comprise materials which will exothermically react together forming an intermetallic compound with the release of at least 7500 gram calories per gram atom.

62. Process according to claim 47 in which said first mentioned powder and said nucleus powder are component pairs selected from the group listed in Tabel I above.

63. Process according to claim 47 in which said first mentioned powder and said nucleus powder are component pairs selected from the group consisting of Al Co, Al Cr, Al Mo, Al W, Al Ta, Al Nb, Al Ti, Al Ni, Si Nb, Si Cr, Si W, Si Co, Si Mo, Si Ni, and Si Ta.

REMARKS

With reference to the first paragraph of page 2 of the Action it is pointed out that the "H V" combination appearing in the Table on page 40 is an obvious error as hydrogen, of course, is not a metal and accordingly this error has been corrected by cancellation.

With respect to the sodium containing combinations it is pointed out that:

a) If the sodium is the nucleus, no problem exists as the cladding protects and isolates the same.

b) The present claims are limited to the process involving the binder and if the sodium is the coating, its incorporation in the binder will sufficiently inactivate the same.

c) In any event the specification is directed to the skilled artisan and it is within the skill of any artisan in the flame spray field to handle reactive powders as it is conventional to handle such powders, such as pyrophoric zirconium and titanium powders which are commonly handled in flame spraying. In connection with sodium the same is only reactive in the presence of water and it is well within the skill of the art to maintain the powder in an inert or dry atmosphere.

Still further, the extension of this objection in connection with claims 48 and 49, as the same are limited to nickel and aluminum powder, is not understood.

The application as originally filed was broadly directed to a very important and basic invention in the flame spray field, i.e. the utilization of composites containing two components which would exothermically react when sprayed forming an intermetallic compound. The concept of flame spraying a composite which in itself generates heat by intermetallic compound formation is entirely novel in the flame spray art, as is a flame spray material capable of performing this function when sprayed. The heat generation by intermetallic compound formation is not to be mistaken nor confused with the spraying of components which will exothermically react by oxidation reaction or thermite-type reaction. The combining of the components into the intermetallic compound upon spraying generates heat which aides and facilitates the spraying process allowing, for example, the formation of self-bonding coatings and the intermetallic compound formed produces a superior and highly desirable coating per se without the introduction of heteroatoms.

One form of the components is the flame spray powder in the form of individually clad particles the nucleus forming one component and the coating the other component. During the initial development of the invention by the applicants it was believed that the coating or cladding of the particles had to be effected by a plating-type operation, such as a chemical plating or vapor deposition. Later the applicants

discovered that the coating could be effected in a much more simple and economical manner by simply dispersing the coating component in a binder applying it to the nucleus component and drying the same. It is not believed obvious that such a coating procedure would have been capable of forming the exothermically reacting powder in accordance with the invention particularly when considering the fact that a mere mixture of individual granules of the components does not produce the exothermically reacting powder in accordance with the invention, no matter how intimate the mixture. It would normally be assumed from this observation that the intimate contacting caused by a true plating would be required and it would be assumed that the coating with the use of the binder might produce a less intimate contact than a simple mixture per se particularly when considering the isolating effect of the binder, such as the varnish.

Nevertheless, the original application was refiled including claims to this particular cladding process and by the requirement for restriction the Examiner has as a matter of law established a patentable distinction as to this particular coating process as compared to the remainder of the invention.

Thus, when considering the patentable merits of the invention it is not proper for the Examiner to consider whether it would be obvious to form a powder such as is claimed in claim 32 by the process of the claims being examined herein, but he must consider the novelty of the claimed process only

taking the cited art into consideration and giving no consideration to the applicants' other claims, etc. In considering the novelty of the process thought must be given to its end result, i.e. the formation of the particular flame spray powder and if the formation of this powder or an equivalent powder is not taught or obvious from the art then the claims must be considered patentable over the art.

It is submitted that neither the formation of the powder claimed formed by the process claims being prosecuted herein, nor the equivalent thereof will result or would be obvious from the teaching of any of the references cited.

The primary reference cited is Hensel et al which relates to the formation of powdered metal bodies such as electric contacts, electrodes, etc. For the formation of the metal bodies Hensel et al teaches the use of a refractory metal coated with palladium, platinum or rhodium utilizing copper, silver or gold as a bonding matrix. The patentee points out that the protective coating of rhodium, platinum or palladium may be effected by initially coating the refractory powder with an adhesive and then dusting thereon with the palladium group metal. Alternately the use of a metal paste as a coating medium is suggested.

None of the metal combinations taught by Hensel et al will produce the flame spray powder claimed by the applicants, or equivalent thereto. Thus none of the combinations taught by Hensel et al, even if in the exact form taught by the applicants of the clad powder would be a flame

spray powder as claimed by the applicants, or equivalent thereof and quite specifically would not be a flame spray powder which when sprayed would form an intermetallic compound with the generation of heat which would aid in the spraying process.

The Examiner's statement that most metals will react exothermically to form intermetallic compounds is challenged and the Examiner is respectfully requested to indicate what combination of metal taught by Hensel et al will act in this manner.

The Joseph and Mackiw et al references had been applied "merely to show the wide variety of metal particles which have been coated with other metals". The portion of the Joseph patent noted by the Examiner, i.e. col. 2, lines 7 to 18 does not relate to coated powder particles, but in contrast thereto relates to an article of nickel, cobalt or chromium alloy which is coated with the finely divided aluminum and silicone in order to render it oxidation and thermal shock resistant. There is no teaching or indication of coated powders which could be used for flame spraying with the production of the applicants' results, or which could be considered equivalent to the powder of the applicant's invention, which exothermically reacts when flame sprayed to form the intermetallic compound.

The Mackiw et al patent relates to a chemical plating process for producing composite powders, but does not teach or relate to an exothermically reacting intermetallic compound forming flame spray powders. While in hindsight it might be possible to pick specific pairs from the large group disclosed in the patent for this purpose, it would not be obvious to make such a specific selection and there is no

teaching or indication directed thereto, and the specific combinations taught in the patent are not suitable and are not equivalent to the claimed combinations.

The Hoyt patent simply teaches the coating of sand with a resin to render the sand suitable for forming a shell mold. There is nothing in this patent which would render obvious the applicants' claimed process of making the specific type of flame spray powder.

It is truly believed that in applying this and the other references the Examiner, at least subconsciously, has been considering the question of patentability on the ground as to whether it would be obvious to form the flame spray powder as basically claimed in the application as filed by the process as claimed herein. Such a standard for determining invention however, is not believed proper in view of the requirement for restriction, and it is further submitted that even if it were, the process would not be obvious for the reasons set forth above.

In view of the above reconsideration and allowance of the claims is hereby solicited.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicant

MAIL ROOM
JUL 13 1965
U.S. PATENT OFFICE

E 549 Metco 305.3

RECEIVED
JUL 14 1965

IN THE UNITED STATES PATENT OFFICE GROUP 160

Applicants : Ferdinand J. Dittrich et al

Serial No. : 343 705 Group 160

Filed : February 10, 1964

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

July 9, 1965

Hon. Commissioner of Patents

Washington, D. C.

Sir:

Supplementing the amendment dated May 18, 1965, please amend the above entitled application as follows:

Page 40, Table 1, column 2, line 5, cancel "B Co" and substitute --B Ca--.

column 4, line 6, cancel "K Te" and substitute --K Ti--.

column 4, line 10, cancel "La Te" and substitute --La Ti--.

REMARKS

Entry of the above amendment is requested to correct obvious errors of a typographical nature in Table I.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By

Attorneys for Applicants

PATENT OFFICE
WASHINGTON

E 550

In Reply Please Refer To: 160

Burgess Dinklage and Sprung
605 Third Avenue
New York, New York 10016

Applicant	
Ferdinand J. Dittrich et al.	
Ser. No.	
343,705	
Filed	
February 10,1964	SEP 24 1965
For	
FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND ETC.	
SHORTENED TIME FOR REPLY	

Cited References Charge Data (If applicable)	
Deposit Account No.	No. of Copies
02-4740	2

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

This is in response to the amendement filed May 19, 1965.

Claims in the case are 47 to 49 and 59 to 63.

Claims 47 and 48 and 59 to 63 are rejected over Hensel et al. per se or further in view of Joseph or Mackiw et al. under 35 USC 103 for reasons applied in the last Office action.

Claim 49 is rejected on the references and reasons applied to claim 47 further in view of Hoyt. This latter reference shows that phenols are known adhesives for particulate material.

Applicants' arguments have been carefully considered but are not deemed persuasive. It's again pointed out that the process of coating a metal powder with an adhesive and coating this substrate with another metal is well known in the art. The particular metals chosen are a mere matter of choice. Also note for Example the Mackiw reference which teaches similar metals as applicants'. Applicants' also urge that it would be unobvious to employ the coated material in flame

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1 - Patent Application File Copy

spraying. It is pointed out that this is not the issue in the case. For Example the powder would have utility in powder metallurgy and more specifically the claims are drawn to the method of making the article and not the article per se or the employment of the particles.

Summary:

Claims non-elected without traverse in paper No. 6: 1 to 46 and 50 to 58.

Claims rejected: 47 to 49 and 59 to 63.

Claims allowed: None

This rejection is made FINAL.

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE FOUR MONTHS FROM THE DATE OF THIS LETTER (804 O. G. 3).

Richard D. Lewis

Examiner
RICHARD D. LEWIS

AGGolian:rme

E 552 Metco 305.3
AS/k

RECEIVED
JAN 27 1966
GROUP 110

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 343 705

Filed : February 10, 1964

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND-FORMING COMPOSITES

January 18, 1966

JAN 4- 1966

Hon. Commissioner of Patents
Washington, D. C.

Group 280

Sir:

The following is in response to the Office Action dated September 24, 1965.

REMARKS

Claims 47 to 49 and 59 to 63 presently under consideration have been rejected under 35 U.S.C. 103, claims 47 and 48 and 59 to 63 being rejected over Hensel et al, or further in view of Joseph or Mackiw, claim 49 being rejected on these references and further in view of Hoyt.

35 U.S.C. 103 provides that a patent may not be obtained if "the subject matter as a whole would have been obvious at the time the invention was made . . .". The applicants' invention as claimed in the rejected claims relates to a process for producing a specific material, i.e. a flame spray powder which has unique characteristics, as for example, is self-bonding. The process as broadly claimed does not simply comprise the application of a coating of a finely divided powder in a binder to a nucleus powder followed by the drying of the binder, but specifically requires the application of a coating powder which is capable of exothermically reacting with the nucleus

powder forming an intermetallic compound. The subject matter sought to be patented as a whole involves the selection of a specific coating powder and nucleus powder, i.e. those which will exothermically react together forming the intermetallic compound. As none of the cited references teach the application of this specific type of coating powder which has this relationship to the nucleus powder, the subject matter as a whole could not have been obvious from the cited art under 35 U.S.C. 103.

The Examiner stated that the particular metals chosen are a mere matter of choice. This statement is vigorously challenged. The crux of the invention resides in this choice of metals and without this choice the applicants' results are not obtained, i.e. the production of the desired flame spray powder or an equivalent product.

The purpose of the process as claimed is to achieve a specific result, i.e. to produce the specific type of flame spray powder. Without this choice of metals, these results would not be obtained.

Stated in another manner, there is nothing in the cited art which would remotely teach or indicate to the skilled artisan a process which would achieve the applicants' results.

In view of the above, reconsideration and allowance of the claims is hereby solicited.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

ADDRESS ONLY THE COMMISSIONER OF PATENTS WASHINGTON D.C. 20231

Paper No. 2

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 554

In Reply Please Refer To: Group 160

Burgess, Dinklage and Sprung

605 Third Avenue
New York, N. Y. 10016

Applicant: Ferdinand J. Dittrich et al.	
Ser. No. 343,705	FILED
Filed Feb. 10, 1964	FEB 25 1966
For FLAME SPRAYING [illegible] CALLY REACTING [illegible] METALLIC COMPOUND FORMING COMPOSITES	

Cited References Charge Data (If applicable)	
Deposit Account No.	No. of Copies

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

This is in response to the letter filed January 21, 1966.

The letter filed January 21, 1966 has been considered in the light of applicants' arguments but no error is seen in the final rejection dated September 24, 1965.

No Notice of Appeal having been timely filed, the case is abandoned.

ALFRED L. LEAVITT
EXAMINER

A.Golian/meb
WO 7-2867

79

MAR 8 1966 PM

ES:LC

E 555

IN THE UNITED STATES PATENT OFFICE

Applicants: Ferdinand J. Dittrich, et al.

Serial No.: 343,705

Filed : February 10, 1964

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Group : 110

March 3, 1966

Hon. Commissioner of Patents
Washington, D.C., 20231

Sir:

The above-identified applicants, by their attorneys, respectfully petition the Hon. Commissioner of Patents in accordance with Rule 137 that the holding of abandonment in this case be withdrawn and that the application be revived and reinstated to the active files of the Patent Office, and, to that end, hereby respectfully represent as follows:

(1) The firm of Burgess, Dinklage & Sprung maintains an effective docket system in accordance with which a Docket Clerk dockets every Office Action received for a date set for response by the attorney who is in charge of the application and for the final date on which the response is due. Each month the Docket Clerk makes a list of cases which are due that month and indicates the date due and the nature of the response, and

80

presents the same to each of the attorneys in the office. In addition, the date for response and the nature of response are indicated on the copy of the Office Action retained in the files. Further, at least two days before each response is due, the Docket Clerk advises the attorney of the response due, and the day before the response is due the Docket Clerk checks and ascertains that the proper response has been filed.

(2) Still further, the Mail Clerk, prior to placing the papers in the envelope for franking and mailing, checks the same for signature, for correct address, and for completeness of the papers with respect to the response.

(3) On September 27, 1965 Mrs. Sara Garcia, the Docket Clerk, on receipt of the Office Action dated September 24, 1965 (Paper No. 11), noted on the Office Action the following: "SPFR (1-24-66)", the same designating that there was a shortened period for response, such response being due January 24, 1966. Copy of page 1 of the above referred-to Office Action is attached hereto. In preparing the docket list for the month of January, Mrs. Sara Garcia entered on the January docket for January 24 the following: "(AS) Metco 305.3 1-24-66 SPFR," the same designating the attorney who was to prepare the response, the case involved (i.e., Metco 305.3 corresponding to Serial No. 343,705), the date for response, and that a shortened period for response had been set. In accordance with office procedure, this indicates a response in the nature of an amendment and is

distinguished from shortened periods for response and Final Actions, which are designated "SPFR and Final" (see attached sheet of office docket).

(4) The case was taken up for action by Mr. Arnold Sprung, the attorney in charge of the case, who, having been advised that a shortened period for response was involved, prepared an amendment which was mailed from the office of the undersigned on January 20, 1966. The Mail Clerk in checking the papers concluded that an amendment was required since only a shortened period for response had been designated on the docket list and sealed the papers for mailing to the Patent Office.

(5) The attorney who prepared the amendment considered the amendment to be a complete response; that a shortened period for response had been set and that it would have been possible had he not considered the amendment to be entirely responsive for the attorney to have obtained an extension of time for up to March 24, 1966, constituting the full six-months' statutory period for response in such situations.

(6) That upon receipt of the Office Letter of February 25, 1966 indicating that the present application had become abandoned for failure to file the Notice of Appeal, the above Petition and supporting Affidavits of Mrs. Sara Garcia and Mr. Arnold Sprung were immediately prepared.

(7) Check to the order of the Commissioner of Patents in the sum of $15.00 in payment of the fee for revival and restoration of the above application is attached hereto. In addition, a check in the amount of $50.00 as required in connection with a Notice of Appeal, together with the Notice of Appeal, is also submitted.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By) _____
Attorneys for Applicants

Mail Book

E 559

Nov. 20, 1966 129

C.O.P.		35	Coburg 284 (N.Y.)
C.O.P.		35	Parker 916 (cancel)
C.O.P.		35	Pecke 2841 (Lightly)
C.O.P.	(U.S. only)	35	Parker 1219 (Rev Case)
C.O.P.	(U.S. only)	35	Metro 3053 (cancel)
C.O.P.		65	Mexico 106 - (Not of list)
C.O.P.		35	Parker 712 (Not of Corp)
C.O.P.		35	Coburg 290 (Not of Corp)
C.O.P.			Coburg 284 (Not of Corp)
C.O.P.		05	Schott 815 (cancel)
C.O.P.			Schott 8151
C.O.P.			Boehringer 227 (N.Y.)
(over) C.O.P.			Pauline 212 (Not of list)
E. L. Reynolds 1st Asst P.M. Gen.		65	
"		35	Parker 1184 (cancel)
C.O.P.		35	
Woodes Inc		35	316 (Rev Case)
Coburg		65	Trendenburg I
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R. Dirkhage (U.S.)		05	Trendenburg 205
Clerk U.S. Ct Customs Pat Appeals			
Pat. Office		65	C 01
Carl Trendenberg		15	I
Boehringer		15	241 Can.
H. L. Ingham		65	Pecke 285
Mobney Chemical		65	Lee Stream (Rev Case)
Dynamit Nobel			284
J. Schoenberg		15	Metro 3054 Clear.
Vereenigde Octrooibureaux		2.10	Princeton 216 Hol.
Hartford Accident		05	C 0
Eastern Airlines		15	C 0
Dr. Kreisler		15	Metro 3054 Clear.
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Docket List

	Zipatex	3	1-20-66	Cert for	1-3-66
	H. Berman	226	1-20-66	Rep Brief	1-12-66
		251-1	"	Rep Brief	1-18-66
	Klee	238	1-20-66	Resp	Allen
	Farben	2336 -3-	1-14-66	Appendix	1-20-66
	Farben	971 C	"	Appendix	1-20-66
	Farben	2171 C	"	Appendix	1-20-66
	Farben	2171	1-25-66	Brief & Appendix	1-20-66
	Farben	310	"	Brief	1-12-66
	Farben	689	"	Brief & Appendix	Filed
	Eschringer	226	"	Appx	Allen filed
	Eschringer	402 22	1-16-66	(Tent. Opp. appx)	filed
	Eschringer	205 (95163)	1-17-66	Brief & Appx transcript	
	Farbwerke	815 Cop 45,154)	"	(Tent. Petition, appx)	Allen filed
	Farben	593	1-19-66	"	1-12-66
	Farben	1003	"	"	1-12-66
	Procter	600	1-20-66	App to CCPA	C.P. file
	Farben	914 (13752)	1-20-66	Stat. Schaffer appx	Filed
	Farben	207 + C. 13.	"	Answer	
	Procter	606	"	Appx	Allen for Eli
	Procter	208	"	Let for Fee	Appx sent
	Gould	231 Canada	1-21-66	Appx	12-16-65
	Berne	269	"	CCPA Ext	1-16-66
	Schering	210	"	Brief & Appx	1-17-66
	Roh	211	"	Appx to CCPA	1-17-66
	Ore Synth.	201	"	Brief Ext	1-20-66
	Durden	42	"	Time Ext	1-14-66
	Procter	703	"	"	1-14-66
	Dynamit	279	1-20-66	Brief & Appx	1-17-66
	Schwarz	221 Cr.	"	Appx	12-17-65
	Pollack	235	"	Brief	Resp Pet. Hamilton
	Procter	764	"	Brief & Appx	Allen
	Ciba	205.1	1-27-66	Brief	1-21-66
	Farbw	1944	"	Brief	1-20-66
	Procter	615-1	"	Brief	1-21-66
	Procter	634	"	"	1-17-66
	Farben	1000	1-25-66	Brief	1-11-66
	Zipatex	273	"	Brief & Appx	1-17-66
	Schurr	232	"	Brief & Appx	Allen
	Procter	764	"	Brief	1-17-66
	Farbw	232	"	Brief	1-21-66
	Farbwerke	227	"	Brief	1-17-66
	Eschringer	227	"	Brief & Appx	1-20-66
	Merck	305.3	"	Brief	1-20-66
	Pollack	231	1-27-66	Reply Brief	1-21-66
	Schering	227	"	Brief & Appx	1-17-66
	Ciba	216	"	Brief & Appx	1-21-66
	Farben	1007	"	Brief (Ext to 2-25-66)	Allen
	Procter	241 Tech	"	Appeal	

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Paper No. 11

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

Metco 305.3

In Reply Please Refer To: 160

Burgess Dinklage and Sprung
605 Third Avenue
New York, New York 10016

Applicant: Ferdinand J. Dittrich et al.	
Ser. No. 343,705	Group
Filed February 10, 1964	SEP 24 1965
For FLAME SPRAYING AND ELECTROSTATICALLY REACTING AN ORGANIC COMPOUND	
ENC. SHORTENED TIME FOR REPLY	

Cites References Charge Data (If applicable)	
Deposit Account No. 02-4740	No. of Copies 2

Please find below a communication from the EXAMINER in charge of this application.

SPFR (1-24-66)

Commissioner of Patents.

This is in response to the amendement filed May 19, 1965.

Claims in the case are 47 to 49 and 59 to 63.

Claims 47 and 48 and 59 to 63 are rejected over Hansel et al. per se or further in view of Joseph or Mackiw et al. under 35 USC 103 for reasons applied in the last Office action.

Claim 49 is rejected on the references and reasons applied to claim 47 further in view of Hoyt. This latter reference shows that phenols are known adhesives for particulate material.

Applicants' arguments have been carefully considered but are not deemed persuasive. It's again pointed out that the process of coating a metal powder with an adhesive and coating this substrate with another metal is well known in the art. The particular metals chosen are a mere matter of choice. Also note for Example the Mackiw reference which teaches similar metals as applicants'. Applicants' also urge that it would be unobvious to employ the coated material in flame

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Stop.

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IN THE UNITED STATES PATENT OFFICE

Applicants: Ferdinand J. Dittrich, et al.

Serial No.: 343,705

Filed : February 10, 1964

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Group : 110

March 3, 1966

AFFIDAVIT

STATE OF NEW YORK)
: ss.:
COUNTY OF NEW YORK)

ARNOLD SPRUNG, being duly sworn, deposes and says that he is a member of the firm of Burgess, Dinklage & Sprung and is admitted to the practice of law in the State of New York and before the Patent Office;

That he is the attorney in charge of the prosecution of the above-entitled application;

That on or about January 18, 1966, in checking the docket for the month of January, he noticed that a response was due in the above case on January 24, 1966, the docket indicating that the necessary response was in the nature of an amendment;

That he prepared such amendment on January 18,1966 and deposited the same with the Mail Clerk;

That immediately on receipt of the Patent Office letter informing that the application had become abandoned

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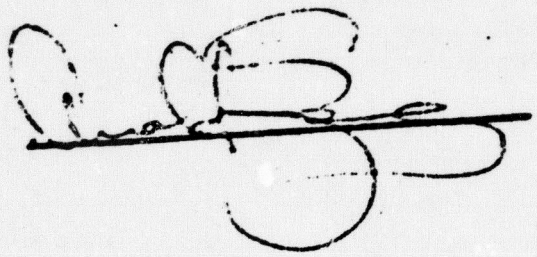
he directed that a Petition in accordance with Rule 137 be prepared.



Sworn to and subscribed before me this 3rd day of March, 1966.

Leila Clapp
Notary Public

LEILA CLAPP
Notary Public, State of New York
No. [illegible]
Qualified in [illegible] County
Commission Expires March 30, 1967

22

MAR 8 1966

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IN THE UNITED STATES PATENT OFFICE

Applicants: Ferdinand J. Dittrich, et al.

Serial No.: 343,705

Filed: February 10, 1964

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Group : 110

March 3, 1966

STATE OF NEW YORK)
: ss.:
COUNTY OF NEW YORK)

SARA GARCIA, being duly sworn, deposes and says that she is the Docket Clerk of the firm of Burgess, Dinklage & Sprung and has held this position for approximately five years;

That on September 27, 1965 she received two copies of an Office Action dated September 24, 1966 (Paper No. 11); that she made note of the fact that a shortened period for response had been set and entered the same and the date for response on the copies of the Office Action as well as on docket cards from which a monthly docket list is prepared; that she did not see or notice that a Final Rejection had been applied;

That it is her usual practice to check the papers again before preparing the monthly docket list but, due to the fact that the January docket list was prepared just before the holidays at a time when the office was very busy, she did not notice that actually a Final Rejection had been applied;

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That she prepared the monthly docket list, copy of which has been attached to the Petition, of which this Affidavit is a part, and that in advising the attorney of the need for response indicated that a shortened period for response only had been set;

That she checked the mail book and noted as an entry on January 20, 1966 that the papers which would have been a complete response, had in fact a shortened period for response only been set, had left the office on January 20, 1966.

Sara Garcia

Sworn to and subscribed before me, a Notary Public, this 3rd day of March, 1966.

[illegible] Clark

Notary Public

LYLA CLARK
Notary Public, State of New York
[illegible]
Commission Expires March 30, 1967

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IN THE UNITED STATES PATENT OFFICE

Applicants : FERDINAND J. DITTRICH, ET AL.

Serial No. : 343,705

Filed : February 10, 1964 Group 110

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Date: March 3, 1966

Hon. Commissioner of Patents
Washington, D.C. 20231

REJECTED CLAIMS: 47-49 and 59-63

(Entry of the amendment of Jan. 18, 1966 for purposes of appeal is hereby respectfully requested)

Sir:

Applicant(s) hereby appeal to the Board of Appeals from the decision of the Examiner finally rejecting the above claims.

Check for $50.00 to cover appeal fee is enclosed.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

BY _____
Attorneys for Applicants

DELAY IN PROSECUTION HELD UNAVOIDABLE (35 U.S.C. 133) PETITION GRANTED

MAR 17 1966

Edwin L. Reynolds
FIRST ASSISTANT COMMISSIONER

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#15

E 567

COPY MAILED S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

MAR 17 1966

March 17, 1966

COMMISSIONER'S OFFICE

In re Application of :
Ferdinand J. Dittrich et al :
Serial No. 343,705 :
Filed February 10, 1964 :

On Petition To Revive

Sir:

The decision of the First Assistant Commissioner on the petition filed in the above entitled application is as follows:

[X] Delay in Prosecution Held Unavoidable (35 U.S.C. 133), Petition Granted March 17, 1966

[ ] Delayed Payment of Final Fee Accepted (35 U.S.C. 151), Petition Granted _____

[ ] Approved _____

[ ] Petition Granted _____

[ ] Petition Denied _____

By direction of the
First Assistant Commissioner

Clarence Thomas

Burgess, Dinklage & Sprung
605 Third Avenue
New York, New York 10016

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E 567-1
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AS/a

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

Appeal No. : 669-58

Filed : March 8, 1966

In re Application of : Ferdinand J. Dittrich et al

Serial No. : 343 705

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Group : 160

May 2, 1966

BRIEF ON APPEAL

The following is an appeal from the Action of the Primary Examiner in the above entitled application dated Sept. 24, 1965, finally rejecting the claims in the above application.

An oral Hearing is respectfully requested.

Kindly charge the brief fee of $50.00 to the account of the undersigned, account No. 02-4740.

THE REJECTED CLAIMS

The rejected claims involved in this appeal are as follows:

47. A process for producing flame spray powder in the form of individually clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and exothermically reacting therewith when melted together forming an intermetallic compound, which comprises applying a coating of a finely divided powder in a binder to a nucleus powder and drying the binder, said first mentioned powder and said nucleus powder comprising materials which will exothermically react together forming an intermetallic compound.

As of MAY 2 1966 fee(s) were applied to

93 Fee Code(s) 1253 50.00 Patent Office

$ (Amount $ given)

48. Process according to claim 47 in which said nucleus is nickel powder and said finely divided powder is aluminum powder.

49. Process according to claim 48 in which the aluminum powder dispersed in a phenolic varnish is admixed with the nickel powder and the varnish dried.

59. Process according to claim 47 in which said first mentioned powder and said nucleus powder comprise materials which will exothermically react with each other when melted together forming an intermetallic compound with the release of at least 3000 gram calories per gram atom.

60. Process according to claim 59 in which said first mentioned powder and said nucleus powder comprise materials which will form an intermetallic compound having a higher melting point than the components.

61. Process according to claim 47 in which said first mentioned powder and said nucleus powder comprise materials which will exothermically react together forming an intermetallic compound with the release of at least 7500 gram calories per gram atom.

62. Process according to claim 47 in which said first mentioned powder and said nucleus powder are component pairs selected from the group listed in Table I (page 40 of spec.) above.

63. Process according to claim 47 in which said first mentioned powder and said nucleus powder are component pairs selected from the group consisting of Al Co, Al Cr, Al Mo, Al W, Al Ta, Al Nb, Al Ti, Al Ni, Si Nb, Si Cr, Si W, Si Co, Si Mo, Si Ni, and Si Ta.

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THE CITED ART

The art cited by the Examiner in support of the Final Rejection is as follows:

2 370 242	2/45	Hensel et al	117-100M
3 102 044	8/63 (9/12/60)	Joseph	117-22
2 853 403	9/58	Mackiw et al	117-100M
2 967 789	1/61	Hoyt	117-100 I

STATEMENT OF APPLICANTS' INVENTION

The application as originally filed is broadly directed to and discloses what is considered a major development in the flame spray field.

Flame spraying, as is well known, involves heating a heat-fusible material such as a metal, to at least heat-softened condition and the spraying, i.e. the propelling of particles of the material in this condition against a surface to be coated. Flame spraying was traditionally effected utilizing a metal as the heat-fusible material and thus is often referred to as "metallizing", though more recently, other materials such as ceramics, etc. are conventionally sprayed.

One of the main problems in flame spraying is the obtaining of a satisfactory bond between the sprayed coating layer and the substrate. Initially in the development of the flame spraying art it was necessary to extensively prepare the surface of the substrate in order to achieve this satisfactory bond. This surface preparation involved an extensive roughening to the extent of undercutting of the surface so that there were actually large

depressions into which the sprayed material would lock in a key-like manner. It was later discovered (see U.S. patent 2 588 421) that molybdenum had the unique property of being able to bond when sprayed without this extensive surface preparation. For some reason the molybdenum would bond satisfactorily to a clean metal surface which had not been extensively surface-roughened and thus the molybdenum could be sprayed as a bonding coat for subsequently applied sprayed layers. Due to this bonding characteristic molybdenum is generally referred to in the art as being self-bonding.

"Thermit"-type powders and materials which would react by an oxidation or oxidation-reduction reaction with the generation of heat were well known for many years, but never found any practical applicability in flame spraying. The generation of the heat by the reaction did not prove advantageous to the spraying reaction and the presence of the oxides inherently involved in the "Thermit"-type reaction was highly undesirable in most flame spray coatings.

The applicants in accordance with the disclosure of the instant application surprisingly discovered that if the flame spray material was in the form of a "composite" containing two components which were capable of exothermically reacting by formation of an intermetallic compound during flame spraying a superior flame spray coat was obtained. The in situ formed intermetallic compound was a highly desirable and superior flame spray coating and the materials were self-bonding and thus could be used without conventional surface preparation required for materials other than molybdenum, and as a bonding coating. The

flame spray material had, however, to be in the form of the "composite" and a mere mixture of the components would not be suitable. Thus, for example, in connection with nickel and aluminum utilized in the form of a powder, the individual powder particles had to be in the form of a composite containing both the nickel and aluminum in intimate contact and a mere mixture of individual powder particles of nickel and aluminum would not be the equivalent and could not be sprayed to form a self-bonding nickel aluminide coating.

In the initial stages of the development the powder particles in accordance with the invention were formed by coating an aluminum nucleus with nickel by a nickel plating method, as for example of the type described in U.S. Patent 2 853 403 of record. Later the applicants discovered that it was not necessary to actually plate the nucleus with the other component metal, but that the same results could be achieved as effectively and more economically by simply in effect forming a "paint" of one of the components and painting the same onto the nucleus. Thus, very finely divided powder of one of the components, such as aluminum was distributed as a pigment in a binder and a coarser powder of the other component, such as nickel, was coated therewith and the binder allowed to dry. After discovery of this novel mode of forming the powder the applicants refiled their application Serial No. 237 786 so as to include and claim this new development.

The Examiner in Paper No. 3, however, required restriction listing this process of forming the powder as a separate invention. In accordance with this requirement the applicants made their election to this invention and thus the claims involved

in this appeal are linited to this process for producing the flame spray powder.

THE CITED ART

The Hensel et al reference relates to a metal composition for forming electrical contacts, the composition being in the form of particles of a refractory metal such as tungsten or molybdenum with a coating of palladium, platinum or rhodium. The coating of the rhodium, platinum or palladium which is a protective coating may be applied by first applying a dispersable adhesive to the refractory powder and then dusting on a powder of the protective metal. This, however, is only a transitory stage in the production and subsequently the material is heated to defuse the protective metal into the surface of the refractory powder. It should furthermore be noted that the refractory metal and the protective coating are not materials capable of exothermically reacting together when melted to form an intermetallic compound.

The Joseph patent teaches the protecting of a metal article by the application of a coating powder onto the surface thereof followed by sintering at low pressure. Col. 2, lines 7-18 specifically mentioned by the Examiner, relates to an article of nickel, cobalt or chromium which is coated with finely divided aluminum and silicon in order to render it oxidation and thermal shock resistant. The chromium powder may initially be applied in a liquid dispersant, but as applied in this form is merely transitory and further converted by the sintering. There is no teaching of application of this powder to other powder particles, but in contrast thereto to an article

such as a turbine blade and no specific combinations are taught which when melted together will exothermically react with the formation of an intermetallic compound.

Mackiw et al relates to a chemical plating process and has apparently been cited by the Examiner "merely to show a wide variety of metal particles which have been coated with other metals". There is no teaching in Mackiw et al relating to the formation of a flame spray powder and no specific teaching of the selection of components which will exothermically react to form an intermetallic compound. While it might be possible to pick specific pairs of materials which could so react from the large group disclosed in the patent, there is no specific teaching or indication to lead to such an arbitrary selection.

The Hoyt patent simply discloses the coating of a granular material such as sand, Carborundum, etc. with a specific binder resin so that the granules may be bound together to form a shell mold for casting.

THE GROUNDS FOR REJECTION

The Examiner has analyzed the rejected claims as simply relating to a process for coating a metal powder by adhesively binding another metal onto the surface thereof, taking the position that the particular metals chosen are a mere matter of choice. The Examiner has specifically taken the position that Hensel et al teaches the coating of powder with an adhesive and the coating of this substrate with another metal. The Examiner has pointed out in his rejection (see Paper No. 7) that since most metals will react exothermically to form intermetallic compounds, the metals of Hensel et al seem to be the equivalent of the applicants'

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metals and that Joseph and Mackiw et al are applied merely to show the wide variety of metal particles which have been coated with other metals. Hoyt has been cited to show that "phenols are known adhesives for particulate materials".

In the Final Rejection (Paper No. 11) the Examiner has summarized his grounds for rejection taking the position that he considers the applicants' invention simply to reside in the physical steps of applying the powdered metal with an adhesive to the metal particles and that the particular metals chosen are a mere matter of choice.

ARGUMENTS

Even if it were assumed for the purpose of argument that the non-elected subject matter of the instant application were prior art so that the particular flame spray powder were known as well as the process of making the same by chemically plating the individual nucleus particles with the exothermically reacting metal coating layer, it is still submitted that the applicants' process would constitute a patentable invention.

As may be noted above, a mere mixture of the components is not operable for producing the exothermically reacting self-bonding flame spray powder as an extremely intimate contact between the components during the spraying operation is required and it was initially believed that the actual plating of one component on the other was required. It is not at all obvious that equivalent results could be achieved by merely bonding finer particles of one component on the particles of the other with a bonding agent, and it is not believed that the Examiner would seriously contend that this type of coating is the equivalent

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to a plated coating. Certainly with the use of a bonding agent in order to effect its bonding function the agent forms an interphase between the two types of particles thus actually preventing a metal to metal contact. The process as claimed is therefore indeed unobvious for producing this particular type of flame spray powder.

The above position is merely set forth to emphasize the error of the rejection and actually need not be considered as the non-elected subject matter does not constitute prior art and in view of the Examiner's requirement for restriction cannot be used as prior art, or in any other manner against the claims involved herein (35 U.S.C. 121).

The claimed process is a process for making a very specific material, i.e. a flame spray powder having specific characteristics. The Examiner's rejection is under 35 U.S.C.103. 35 U.S.C. 103 provides that a patent may not be obtained if "the subject matter as a whole would have been obvious at the time the invention was made". The subject matter as a whole does not, as the Examiner contends, simply relate to a process of coating a metal powder with an adhesive and coating the substrate with another metal. As a very integral and important part of the subject matter as a whole is the relationship between the two metals, i.e. the same must be capable of exothermically reacting forming an intermetallic compound, the selection of these metals must be considered a critical part of the claimed invention and process. Thus, as contrasted to the Examiner's over simplification of whatever he considers the invention, the invention resides in not simply coating a metal by adhesively

binding a metal powder as a coating on another metal, but includes the selection of the two components as metals which are capable of exothermically reacting with each other to form an intermetallic compound. Without this selection of these specific components it is not possible to produce a flame spray powder which is the very object of the invention and process. The particular metals chosen are therefore not a matter of choice, but their particular selection as specific components used in the process constitutes the very heart of the invention of claimed.

The capability of metal pairs to exothermically react forming an intermetallic compound is not a property which is common or general among metals and only selected combinations have this unique characteristic.

None of the references cited by the Examiner teach the formation of composite particles containing two separate metals which are capable of so exothermically reacting. Thus, there is absolutely no teaching in any of the references or any combination thereof which could render the subject matter of the applicants' claimed invention obvious as a whole. The rhetorical question is asked: How could the subject matter of the claimed invention be obvious from the references when there is no teaching in the references which would enable the obtaining of the object of the invention and process, i.e. the specific flame spray powder? As pointed out, Hensel et al's particles are merely transitory in his process and even in this transitory stage cannot be considered anticipatory as the components which will exothermically react are not present nor taught. None of the secondary references teaches this selection of the specific types of components which

are capable of so exothermically reacting, and furthermore, none of the references are such as would allow in combination with Hensel et al a substitution of a component used by Hensel et al for a corponent used in the references.

It is submitted that the Examiner's true grounds of rejection have actually subconsciously involved a consideration of the applicants' own basic invention, i.e. the flame spray powder composite containing the exothermically reacting components. It appears that the Examiner has considered that once these composites are known, the formation thereof by the particular claimed process would be obvious. Such grounds for rejection, are however, not proper. The applicants' had initially combined the claimed process in a single application which is broadly directed to the inventive concept of the use of the composite containing the exothermically reacting intermetallic corpound forming components. The claims involved herein are only being prosecuted apart from the other claims as a result of the Examiner's own requirement for restriction. In view of this requirement for restriction the Examiner is precluded from consideration as to whether the claimed process is patentabily distinct from the generic invention or powder per se, or whether the process constitutes an obvious method of the making of the claimed material. In determining patentability it is only proper that the subject matter as a whole be considered apart and completely independent of any other concept disclosed or claimed in the application. A main point of novelty in this subject matter as a whole is the specific selection of the components as the result sought from this process can only be achieved with such selection. As the

cited art is completely devoid of any teaching of such selection the Examiner's rejection under 35 U.S.C. 103 is obviously in error and should be reversed.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

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U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 579

In re application of

Ferdinand J. Dittrich et al.

Ser. No. 343,705
Filed February 10, 1964
For FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Appeal No. 669-58

Before the Board of Appeals

AUG 14 1958

GROUP 130

Burgess, Dinklage & Sprung, for Appellant

Examiner's Answer

This appeal involves claims 47 to 49 and 59 to 63. A correct copy of the appealed claims appears on pages 1 and 2 of applicants' Brief.

THE REFERENCES OF RECORD RELIED ON ARE:

Hensel et al.	2,370,242	February, 1945	27
Mackiw et al.	2,853,403	~~October~~ September, 1958	23
Hoyt	2,967,789	January, 1961	10
Joseph	3,102,044	September, 1963 (filed 7-12-60)	27

BRIEF DESCRIPTION OF THE INVENTION

The present invention is concerned with the method of applying a coating of a finely divided metal powder in a binder to a nucleus metal powder and drying the binder. The specific combination of metallic powders are chosen such that these powders

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will have the capability of exothermically reacting to form an intermetallic compound. The utility of the product formed by the process of the claimed invention is in flame spraying wherein the sprayed powders exothermically react to form an intermetallic coating upon a substrate.

BRIEF DESCRIPTION OF THE REFERENCES

Hensel et al. relates to metal powder compositions made from refractory metal powders, such as tungsten and molybdenum, which are coated with protective layers from members of the palladium-platinum group metals. These compositions are bonded together with a metal such as copper, silver or gold. The protective coating may be applied by many conventional techniques including coating the powder with a dispersible adhesive and then dusting the protective metals in powder form. Subsequently the coating powders are heated to disperse the adhesive and diffuse the protective metal into the surface of the refractory powders.

Heckle et al. teach a method of producing metal composite powders of two or more metals comprising

suspending by agitation metal particles in a ammoniated solution to form a slurry. A metal having physical and/or chemical properties different from those of the dispersed metal is present in the solution as a soluble salt. The solution is reacted with a reducing gas under pressure at an elevated temperature to precipitate from the solution particles of metal in elemental form on the dispersed metal particles.

Hoyt teaches a method of bonding granular material such as sand, resins or glass with a phenol-aldehyde resin.

Joseph teaches a process for applying a protective coating of refractory metal, alloys, oxides or mixtures from a finely divided powder or dust upon a metal or alloy substrate. The powder may be applied to the substrate by blasting, dusting, or dispersing in a liquid solvent. After coating the coated article is sintered at elevated temperatures under reduced pressure.

REJECTION

Claims 47, 48 and 59 to 63 stand rejected as

unpatentable over Hensel per se or further in view of either Joseph or Mackiw et al. under 35 U.S.C. 103. Hensel et al. teach the process of coating a metal powder with an adhesive and then coating another metal powder with this composition. Also the metal coating may be applied in the form of a paste. (page 1, right hand column, lines 46 to 55). Since most metal will react exothermically to form intermetallic compounds, the metals of Hensel et al. are seen to be equivalent to Applicants' metals. In any case the Joseph and Mackiw et al. references are applied to show a wide variety of metal particles which have been coated with other metals. (For example, column 2, lines 7 to 18 and first complete paragraph of column 3 of Joseph). Mackiw also teaches the claimed combination of Al-Ni in claims 45, 49 and 63. (column 2, lines 16 and 24). It would be obvious to one skilled in the art to employ the process of Hensel et al. per se or further employ other different metal components as shown by Joseph or Mackiw et al.

Claim 49 is rejected over Hensel per se or further in view of either Joseph or Mackiw et al.,

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each rejection taken further in view of Hoyt under 35 U.S.C. 103. Dependent claim 49 differs over parent claim 47 only in claiming a specific binder namely phenolic varnish. Hoyt is applied only to teach that when bonding a granular material, phenol resins are known adhesives. To employ the adhesive of Hoyt as the adhesive taught generally by the combination of the references applied to claim 47 is seen obvious.

RESPONSE TO ALL ARGUMENTS IN THE BRIEF

Applicants urge that the rejection of the appealed claims is improper since under 35 U.S.C. 103 "the subject matter as a whole would have been obvious at the time the invention was made." Applicants then urge that the choice of a metal powder as a coating of another metal is predicated on the ability to exothermically react with one another to form an intermetallic compound. Contrary to applicants' assertion on page 10, lines 10 to 13 of the Appeal Brief, this capability of exothermically reaction by two metals to form an intermetallic compound is a common and general property of the combining metals. Hence the application of Hensel et al.

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is seen to be proper. Furthermore direct issue is taken that the claimed combination of metals is not shown by the applied references. For example in the figures (1 to 5) of the drawings of the specification, the combination of aluminum-nickel is set forth. This claimed combination is also found in the claims (1, 17 and 53). Hackh et al. at column 2, lines 17 and 3, respectively teach composite metal powders of aluminum-nickel. The intended use of the powder, namely in a flame spray process is not seen to be an issue in the case. Claims at the instant application drawn to the method of flame spraying process were non-elected, the requirement for restriction being set forth in Paper No. 3 and the election made in Paper No. 5. Therefore to employ the conventional process of binding metal powders to one another with powders previously employed in the art is seen to be well within the ordinary skill of one in the art. The particular adhesive chosen (claim 49) is a question of choice and applicants do not urge unobvious criticality in the choice of such a resin. Applicants' remaining argument centers in the fact that the particles of the primary Hensel et al.

Serial No. 343,705
Attorney No. [illegible]

reference are transitory since metal powder combination of the reference is ultimately bonded to form an article. It is pointed out that the claims of Hensel et al. are drawn specifically to a metal powder composition. It appears that the way the applicants are employing the word "transitory" is that all metal powders are "transitory" if they have utility to form a different and distinct product. Applicants' powder is transitory in the light of this definition since his disclosed utility would be ultimately in a flame spray process that produces a fused intermetallic coating that differs from the employed powder.

For the reasons given above, it is submitted that the Final rejection of claims 17 to 29 and 50 to 63 is proper, and it is respectfully urged that the rejection be affirmed.

Respectfully submitted,

ALFRED L. LEAVITT
Examiner, Group 260

ALL:ec
[illegible]

111

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U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

Paper No. 28

E 586

August 23, 1966

C

Burgess, Dinklage & Sprung
665 Third Ave.
New York, N.Y. 10016

Appeal No.: 669-58
Appellant: Aitrich, F.J., et al
Serial No.: 343,765

Hearing
Date: Nov. 8, 1966
Time: 1:00 PM
Place: 2121 Rhode Island Ave.
Fifth Floor

NOTICE OF HEARING
CONFIRMATION REQUIRED WITHIN TWENTY DAYS

The appeal in the above identified case will be heard by the Board of Appeals on the date indicated.

The hearings will commence at the time set and as soon as the argument in one case is concluded, the succeeding case will be taken up.

The time allowed for argument is thirty minutes unless additional time is requested and permitted before the argument is commenced.

By Order of the Board of Appeals.

Mary S. Olkowski

Acting Administrative Officer

NOTE: In order to make the most effective use of the Board's hearing facilities, CONFIRMATION OF THE REQUEST FOR ORAL HEARING, WHICH HAS BEEN SET AS NOTED ABOVE, IS REQUIRED WITHIN TWENTY DAYS FROM DATE OF THIS NOTICE.

Failure to do so will be construed as a waiver of the request for the hearing.

PLEASE REFER TO APPEAL NUMBER IN ALL COMMUNICATIONS CONCERNING THIS CASE

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POL.-88 (4-66)

USCOMM-DC 62643-P66

BOARD OF APPEALS
AUG 24
U.S. PATENT OFFICE

AUG 19 1966
U.S. PATENT OFFICE

Metco 365.3
AS/a

E 587

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

Appeal No. : 669-58

Filed : March 8, 1966

In re Application of : Ferdinand J. Dittrich et al

Serial No. : 343 705

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Group : 160

August 16, 1966

REPLY BRIEF

In the Examiner's brief the Examiner states (page 5, last paragraph) " . . this capability of exothermically reaction by two metals to form an intermetallic compound is a common and general property of the combining metals." The Examiner cites absolutely no authority and provides no basis for this statement and this statement is challenged as being manifestly incorrect. The ability of metal pairs to react exothermically forming an intermetallic compound is not a common, but quite contrary, an uncommon and extraordinary characteristic of metals. The Board can take judicial notice that of all known metals there are literally millions of combinations possible. Yet of this vast universe of possible combinations the table as given on pages 40 and 41 of the applicants' specification, is to the best of the applicants' information and belief a fairly comprehensive list of possible useful combinations which will so exothermically react in forming an intermetallic compound. The applicants during prosecution of the application (paper No. 8, page 7, first full paragraph) specifically challenged this statement of the Examiner and specifically

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requested that the Examiner indicate what combination of metals taught by Hensel et al would act in this manner. As the Examiner had never responded to this challenge or cited authority, it is submitted that the Examiner's statement cannot be given any weight and, in fact, the Board can take judicial notice that the same is inaccurate.

The Examiner furthermore in his brief sets forth that Mackiw et al in column 2, lines 17 and 34 respectively, teach composite metal powders of aluminum and nickel. An examination of this cited portion of the Mackiw et al patent, however, clearly shows that there is no teaching or mentioning of such an aluminum-nickel composite metal powder and contrary thereto there are simply two large groups of metals from which the aluminum and nickel would have to be specifically selected with no teaching toward such selection.

The Examiner further states that the claims of Hensel et al are specifically drawn to a metal powder combination. This is incorrect. The claims of Hensel et al are directed to a composition formed of particles of a refractory metal which are coated with another metal and in which the particles are bonded together with copper, silver and gold. Aside from this bonding together the coated particles have no relation to a coating in the sense of the applicants' process, but the coating is a sintered coating and not an adhesive bonded coating. The adhesive bonding is not covered in the claims and, as pointed out, is transitory in that it is only used to position the palladium-platinum group metal for the sintering and the coated particles which are recovered to be bonded together to form the claimed composition have no relation to the applicants' invention and are particles with a sintered coating.

It is respectfully urged that the Examiner's rejection be reversed.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

MAIL ROOM SEP 7 1966 U.S. PATENT OFFICE

E 590

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

Appeal No. : 669-59

Filed : March 8, 1966

In re Application of : FERDINAND DITTRICH, ET AL.

Serial No. : 2[illegible]

Filed : February 12, 1964

For : FLAME SPRAYING THERMOCHEMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

BOARD OF APPEALS
SEP 1 [illegible]
U.S. PATENT OFFICE

Group : 160

September 6, 1966

NOTICE OF CONFIRMATION

The undersigned attorneys hereby confirm the request for Oral Hearing in the above entitled Appeal.

Respectfully submitted,

BURGESS, DINKLAGE AND SPRUNG

By: [signature]
Attorneys for Applicants

Group 160 Paper No. 21

E 591

Appeal No. 669-58

Hearing:
November 8, 1960

DEC 21 1960
U.S. PATENT OFFICE
BOARD OF APPEALS

IN THE UNITED STATES PATENT OFFICE

BEFORE THE BOARD OF APPEALS

Ex parte Ferdinand J. Dittrich
and Arthur F. Shepard

- - -

Application for patent filed February 10, 1954, Serial No. 343,705. Flame spraying exothermically reacting Intermetallic Compound forming Composites.

Burgess, Dinklage & Sprung for appellants.

Before Asp and Nagil, Examiners-in-Chief, and Rebold, Acting Examiner-in-Chief.

Rebold, Acting Examiner-in-Chief.

This appeal is from the final rejection of claims 47, 48, 49 and 59 through 63. No claim has been allowed. Claims 1 through 46 and 50 through 58 are not before us, being withdrawn under Rule 142(b).

The appealed claims concern a method for coating metal powder (e.g., nickel) with a different metal powder

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(e.g., platinum). Claim 47 is representative:

47. A process for producing flame spray powder in the form of individually clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and exothermically reacting therewith when melted together forming an intermetallic compound, which comprises applying a coating of a finely divided powder in a binder to a nucleus powder and drying the binder, said first mentioned powder and said nucleus powder comprising materials which will exothermically react together, forming an intermetallic compound.

The references of record are:

Hensel et al.	2,270,242	Feb.	27, 1945
Mackiw et al.	2,853,402	Sept.	23, 1958
Boyt	2,967,789	Jan.	10, 1961
Joseph	3,102,[illegible]	Sept.	[illegible], 1963
		(filed 9-12-[illegible])	

Reference added to show state of the art:

Grala et al. 2,910,356 Oct. 27, 1959

Claims 47, 48 and 59 through 63 stand rejected as unpatentable over Hensel et al. alone or in view of either of Joseph or Mackiw et al. The primary reference discloses powdered tungsten or molybdenum coated with up to 90% of the total weight of powdered rhodium, platinum or palladium. A variety of coating methods are described, one of which uses a metal paste, and another a powdered adhesive for holding the coating powder on the nucleus particles. The examiner apparently believes that the pairs of powders in Hensel et al. inherently have the property of exothermically forming an intermetallic compound upon fusion (despite appellants' contrary contention). The examiner cites the secondary references to show a wide variety of metal particles which have been coated with other metals.

Appellants deny that any of the coated particles in Hensel et al. are capable of exothermically forming an intermetallic compound. They point out (correctly, we think) that Joseph does not apply his coating to a powder, but to a

massive surface, such as a turbine blade. Their objection to the Mackiw et al. patent is that it lacks any express teaching of exothermically forming any intermetallic compound, or of a specific pair of metal powders for which this would be inherent.

We have carefully reviewed all of appellants' arguments, but find no reversible error in this rejection. Process claims of the present type cannot rely for patentability on any novelty in the article produced by the process; In re Neuerbauer et al., 51 CCPA 1139, 1964 C.D. 5, 83 C.D. 935, 330 F.2d 353, 141 USPQ 205. Nor can a method claim for preparing an alloy distinguish merely in the composition of the alloy; In re Becket et al., 24 CCPA 992, 1937 C.D. 384, 483 C.D. 471, 88 F.2d 684. Accordingly, we find that the manipulative steps of these claims are essentially those of Hensel. The metal paste in the latter could obviously include a binder, as done in Joseph, column 3, lines 8-21. We see little merit in appellants' contention that Hensel's coated particles are "merely transitory". This would appear to be also true of appellants' powder, since in both cases the powders are converted to another material.

We are not impressed by appellants' challenge of the Examiner's assertion concerning intermetallic compounds, because appellants' specification states on page 7 that "an extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat." The Grala et al. patent is added to the record to show that aluminum and nickel are known to form a compound NiAl with

Appeal No. 669-58

high exothermic heat development, and the compound has a higher melting point than Al or Ni (column 1, lines 25-35). It is clear from Mackiw et al. that composite binary coated powders are well known (column 1, lines 35-39), and we find a teaching therein that aluminum powder can be coated with nickel (column 2, lines 16 and 34). With respect to the details added in claims 59, 60 and 61, we note that the specification fails to disclose which specific pairs of metals possess these properties.

Claim 49 stands rejected on the same art discussed above, in further view of Hoyt. The latter shows that phenolic compounds are well known bonding agents for discrete granular materials. It is clear that this dependent claim stands or falls with its parent claims 47 and 48. This rejection will be sustained for the same reasons applied above to the parent claims.

The decision of the examiner is affirmed.

AFFIRMED

Examiner-in-Chief

Examiner-in-Chief

Examiner-in-Chief
(Acting)

BOARD OF APPEALS

Burgess, Dinklage & Sprung
60[illegible] Third Ave.
New York, N.Y. - 10016

ATTORNEY'S ROOM

MAR 12 1968

U. S. PATENT OFFICE

E 595

Hon Commrs of Patents:

Your petitioner requests access to the file of abandoned application Serial No. 343,705, filed Feb 10, 1964 and referred to in US Patent 3322515.

Steven Goldby
3/12/68

APPROVED
MAR 12 1968

ATTORNEY'S ROOM

E 596

April 22,1968

Hon. Commissioner of Patents

Washington, D. C. 20231

S I R :

PETITION FOR ACCESS

The undersigned hereby petitions for access to the file of abandoned application Serial No. 343,705, filed February 10, 1964.

This application is mentioned in U. S. Patent 3,327,515, issued May 30, 1967.

Access to this application is necessary in order to determine the scope and validity of the claims of the issued patent.

Respectfully,

SHOEMAKER AND MATTARE

By John F. Smith

Approved
4/24/68
D. R. Plummer

122 12

E 597

Form PO-88a

3437705

Asst. No. Serial No.

Assistant examiner

Division No. 117

Appl

RECEIVED

JUN 1 6 1964

GROUP 180

See Caveat 237786

SEARCHED

Class	Sub	Date	Ex'r
117	100 M 100 L	3/65	CW
Searched in 237,786			
117	105.2 46 F 3		
29	191 192 194		
75	0.55		
117	21 105		
Signing Ass. Book No. 110			
Abandoned		7/65	CW
Book Out		7/66	CW

INTERFERENCE SEARCHED

Class	Sub	Date	Ex'r

INDEX OF CLAIMS

Claim	Date	Claim	Date
1	7/65	21	7/65

SYMBOLS

STATUS

See 2,910,304 2,334,480

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75

3437O5

APPEAL NO. 669 58

E 598

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16—11270-6 U.S. GOVERNMENT PRINTING OFFICE

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